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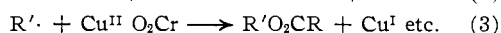
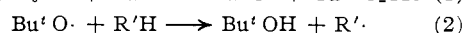
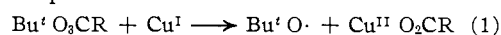
Reactions of Benzoyl Peroxide and Olefins Catalyzed by Copper Salts¹BY JAY K. KOCHI^{1a}

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Benzoyl peroxide reacts with olefins in the presence of copper salts to form benzoate esters and benzoic acid as described by Kharasch and Fono. This reaction is compared to the analogous reaction employing *t*-butyl peresters. The difference in composition of products obtained with each peroxide is attributed to the formation of benzoxy radicals from benzoyl peroxide and *t*-butoxy radicals from *t*-butyl peresters with copper salts. Benzoxy radicals react with olefins primarily by addition, whereas *t*-butoxy radicals react by hydrogen abstraction. Products are formed as a consequence of the facile cupric salt oxidation of the ensuant radicals, benzoxyalkyl adduct radicals and alkenyl radicals, respectively. The relative rates of addition to and hydrogen abstraction from butenes by benzoxy radicals is discussed. Evidence is presented for the formation of benzoxybutyl radical intermediates.

Introduction

The copper salt-catalyzed reaction of *t*-butyl peresters and olefins was described in a previous paper.² The reaction was postulated to proceed *via* the steps



The isomeric butenes (butene-1, *cis*- and *trans*-butene-2) and *t*-butyl peresters (acetate and benzoate) with copper salts as catalysts (0.5%) produced the same mixture of α -methallyl (~90%) and crotyl esters (~10%). The reactions conducted in *n*-hexane and benzene solvents were not homogeneous due to the low solubility of the copper salts. The relative yields of α -methallyl and crotyl esters formed under these conditions did not differ significantly from those obtained in the completely homogeneous media (acetonitrile, methanol and acetic acid). However, in the presence of excess cupric salts (~2%) the homogeneous systems afforded a mixture consisting mainly of the α -methallyl ester (95–100%) with only small amounts of crotyl isomer (< 5%).

In similar reactions, Kharasch and co-workers first described the copper salt-catalyzed reaction of octene-1 with *t*-butyl peresters³ and with benzoyl peroxide.⁴ Although the former was reported to yield exclusively the unrearranged 3-acyloxyoctene-1, the latter yielded a mixture of allylic isomers, 3-benzoyloxyoctene-1 and 1-benzoyloxyoctene-2 in approximately equal amounts, in addition to benzoyloxyoctanes and phenylated materials. The resolution of this apparent anomaly between the behavior of *t*-butyl peresters and benzoyl peroxide toward olefins and an elaboration of the mechanism of these interesting reactions is the subject of this paper.

Results

The isomeric butenes were chosen as representative olefinic substrates for study because of the accessibility and unequivocal structure assignments

(1) Presented in part before the Petroleum Section of the Gordon Research Conference, Colby Junior College, New London, N. H., June, 1961. Part II, Peroxide Reactions Catalyzed by Copper Salts. For previous papers see *J. Am. Chem. Soc.*, **83**, 3162 (1961), and publication in press.

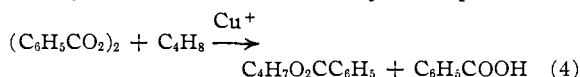
(1a) Department of Chemistry, Case Institute of Technology, Cleveland 6, Ohio.

(2) J. Kochi, *J. Am. Chem. Soc.*, **84**, 1193 (1962).

(3) M. Kharasch, G. Sosnovsky and N. Yang, *ibid.*, **81**, 5819 (1959).

(4) M. Kharasch and A. Fono, *J. Org. Chem.*, **24**, 606 (1959).

of their derivatives. The copper salt-catalyzed reaction of benzoyl peroxide and butenes taken in analogy with the reactions of *t*-butyl peresters ideally should be describable by the equation



The subsequent reactions will be discussed in terms of this stoichiometry.

Butene-2 and Benzoyl Peroxide.—A solution of benzoyl peroxide and *cis*-butene-2 in benzene reacted when heated at 70–80° for 24 hours to yield benzoic acid (20%) and a mixture of esters (180%)⁵ (see run A, Tables I and II). The ester products for this *uncatalyzed* reaction consisted of a 94% yield of *sec*-butyl benzoate, 3% of α -methallyl benzoate and 28% of octyl benzoate (2-benzyloxy-3,4-dimethylhexane). Unidentified higher molecular weight esters were formed in 59% yield. The recovered unreacted butene was unrearranged.

A reaction carried out under similar conditions in the presence of catalytic amounts of copper salts (cuprous chloride, cuprous bromide, cupric acetate) yielded different results. There was formed in 75–85% yield a C₄-benzoate mixture (mainly α -methallyl and *sec*-butyl benzoates) together with 80–85% benzoic acid, 30% unidentified higher molecular weight benzoates and a small amount (< 1%) of biphenyl and also some C₄-benzenes. Less than 5% C₈-benzoates were formed in these *catalyzed* reactions.

In Table I the yields of benzoic acid, C₄-benzoates and higher molecular weight esters formed under representative conditions are listed. In most cases there were good material balances among these compounds and the benzoyl peroxide charged. The yields of carbon dioxide were not measured, but in all the catalyzed reactions little gaseous products were apparent. The unreacted butene-2 was isolated in each case and examined for rearrangement and isomerization. Butene-1 was not formed. Only when cuprous bromide was employed as a catalyst was *cis-trans* isomerization observed. Neither cuprous chloride nor cupric acetate induced the isomerization; the results were otherwise the same as those obtained from the cuprous bromide catalyzed reactions.

Competition experiments were conducted using a fivefold excess of *cis*- and *trans*-butene-2 mixtures. The unreacted butene-2 was reisolated and re-

(5) Yield calculations are based on a mole of benzoyl peroxide producing a mole of benzoic acid and a mole of benzoate ester.

TABLE I
 COPPER SALT CATALYZED REACTION OF BUTENE-2 WITH BENZOYL PEROXIDE

Run	Butene-2, g.	Solvent, ml.	Benzoyl peroxide, g.	Copper salt, g.	Benzoic acid, ^a % (g.)	C ₄ -Benzoate ^b	High mol. wt. ^c ester, %	Σ, ^d %
A	<i>cis</i> (52)	Benzene (75)	15.3	None	21	97	59 ^e	89
B	<i>cis</i> (53)	Benzene (75)	23.7	CuBr (0.161)	84 (8.1)	74	33	95
C	<i>trans</i> (50)	Benzene (75)	23.0	CuBr (0.163)	85 (8.4)	78	33	98
D	<i>cis</i> (55)	Benzene (75)	20.6	CuCl (0.205)	74 (7.6)	88	21	92
E	<i>cis</i> (55)	Benzene (75)	20.2	Cu(OAc) ₂ (0.305)	82 (7.6)	87	29	99
F	<i>cis</i> (56)	<i>n</i> -Heptane (100)	23.7	CuBr (0.155)	61 (7.1)	85	44	95
G	<i>cis</i> (52)	<i>n</i> -Heptane (100)	22.3	CuBr (0.214)	(7.0)	89	41	..
H	<i>cis</i> (53)	{ Benzene (75) Acetic acid (25)	16.9	CuBr (0.165)	(10.1)	91	11	..
J	<i>cis</i> (55)	Acetonitrile (100)	24.1	CuBr (0.165)	93 (9.8)	89	12	97
K	<i>cis</i> (56)	Acetonitrile (100)	24.3	{ CuBr (0.205) Cu(OBz) ₂ (1.241)	100 (11.7)	85	14	99
L	<i>cis-trans</i> (35.0) ^f	Acetonitrile (100)	24.8	{ CuCl (0.302) Cu(OBz) ₂ (1.996)	96 (13.2)	89	10	98
M	<i>cis-trans</i> (35.6) ^g	Benzene (75)	24.8	CuCl (0.331)	84 (8.3)	77	27	94

^a Determined by potentiometric titration; weight of benzoic acid isolated in parentheses (not quantitative). ^b Determined by G.L.C. marker. ^c Difference between total saponification value and C₄-ester by marker. ^d Material balance; percentage of peroxide charged accounted for as benzoic acid and benzoate esters; remainder is phenylated butenes, benzene, etc. ^e Includes 28% 2-benzyloxy-3,4-dimethylhexane. ^f Reactant butene is 38.4% *trans* and 61.6% *cis*; recovered butene-2 is 40.0% *trans* and 60.0% *cis*. ^g Reactant butene is 64.6% *trans* and 35.4% *cis*; recovered butene-2 is 67.6% *trans* and 32.4% *cis*.

analyzed. The *cis* isomer was found to be consumed 2.1 times faster than *trans*-butene-2 in acetonitrile and 1.8 times faster in benzene.

The reactions in benzene and *n*-heptane were not homogeneous in copper salt catalyst. After completion of the reaction most of the copper salt charged was present as insoluble cupric benzoate. The heptane solutions were pale blue and the benzene solutions slightly bluer, qualitatively indicating a higher cupric salt concentration in the latter system. The reactions in acetonitrile and acetic acid-benzene solvents were completely homogeneous. The reaction mixtures varied from dark green to blue depending on the solvent and cupric salt concentration.

The results presented in Table I indicate that solutions (acetonitrile and acetic acid-benzene) containing higher cupric ion concentrations approach the ideal stoichiometry, *viz.*, one equivalent of benzoic acid and one equivalent of C₄-benzoate for each mole of benzoyl peroxide charged, as given in eq. 1.

The accompanying change in the composition of the C₄-benzoate mixture under these conditions is shown in Table II. The formation of butenyl benzoates also parallels the approach to ideal stoichiometry. The side reactions represented by the *cis-trans* isomerization of the reactant 2-butenes (with cuprous bromide) and the formations of *sec*-butyl benzoate and higher molecular weight esters decrease concomitantly. In these reactions containing relatively high cupric salt concentrations (acetonitrile and acetic acid-benzene solvents), the butenyl benzoate mixture formed in high yield consisted predominantly of the α -methallyl isomer. Thus, in the presence of added cupric benzoate, α -methallyl ester is formed uncontaminated with crotyl benzoate (<0.1%) and *n*-butyl benzoate (<2%). In acetic acid-benzene mixed solvent part of the ester product was identified as a mixture of butenyl acetates (predominantly α -methallyl iso-

 TABLE II
 COMPOSITION OF C₄-ESTERS FROM BUTENE-2

Run ^a	Over-all yield C ₄ -benzoates, %	% composition of C ₄ -benzoates— α -Methallyl	Crotyl	<i>sec</i> -Butyl	Recovd. butene-2, % <i>cis</i>
A	97	3	<0.1	98	~99
B	74	78	4	18	48
C	78	78	6	16	26
D	88	75	3	22	~99
E	87	78	3	19	~99
F	85	51	7	42	35
G	89	53	7	40	38
H	72	91	<0.1	9	75
	19 ^b	95	5	0	
J	88	92	1	7	83
K	85	98	<0.1	2	81
L	89	98	1	1	60
M	77	77	5	18	32

^a See Table I. ^b Butenyl acetate fraction.

mer) in addition to α -methallyl benzoate. No butyl acetates were found.

Butene-1 and Benzoyl Peroxide.—Benzoyl peroxide reacted with butene-1 under conditions identical to those employed for butene-2. The uncatalyzed thermal reaction of benzoyl peroxide and butene-1 produced 47% benzoic acid, 22% mixture of C₄-benzoates, (see run N, Tables III and IV) 17% 1-benzyloxy-2-ethylhexane (no octenyl benzoates) and 57% higher molecular weight unidentified esters. In the presence of copper salts the composition of products and their yields are altered drastically. Even in the copper salt catalyzed reactions, however, C₈-benzoates are significant products, as contrasted to the reactions with butene-2.

In Table III, the stoichiometries under various conditions are listed. The over-all yields of combined C₄-esters and C₈-esters from butene-1 were consistently lower than those from butene-2, the difference lying primarily in the greater yields of

TABLE III
 COPPER SALT CATALYZED REACTION OF BUTENE-1 WITH BENZOYL PEROXIDE

Run	Butene-1, g.	Solvent, ml.	Benzoil peroxide, g.	Copper salt, g.	Benzoic acid, ^a % (g.)	C ₄ -Benzoates, ^b %	C ₈ -Benzoates, %	High mol. wt. benzoates, % ^c
N	53	Benzene (75)	15.1	None	46 (3.2)	22	17	57
P	54	Benzene (75)	24.0	CuBr (0.153)	24	23	28
Q	51	Benzene (100)	25.9	CuBr (0.222)	29	21	25
R	48	<i>n</i> -Heptane (100)	22.1	CuBr (0.204)	84 (8.9)	34	20	29
S	53	Benzene (75) Acetic acid (25)	24.4	CuBr (0.202)	(14.4)	42 ^d	23	23
T	53	Benzene (50) Acetic acid (50)	22.1	CuCl (0.201) Cu(OBz) ₂ (1.498)	(13.8)	55 ^d	7	15
U	53	Acetonitrile (100)	22.0	CuCl (0.202) Cu(OBz) ₂ (1.490)	(10.1)	51	10	16

^a Titrated yield of benzoic acid; isolated weight in parentheses; not quantitative. ^b By G.L.C. marker technique. ^c Difference between total saponification value and C₄-C₈-benzoates. ^d Includes C₄-acetates.

 TABLE IV
 COMPOSITIONS OF C₄- AND C₈-BENZOATES FROM BUTENE-1

Run ^a	Over-all yield C ₄ -benzoates, %	% composition of C ₄ -benzoates				Over-all yield C ₈ -benzoates, %	% composition of C ₈ -benzoates	
		Crotyl	α -Methylalyl	<i>n</i> -Butyl	<i>sec</i> -Butyl		Octyl ^b	Octenyl ^c
N	22	0	34	50	16	17	100	0
P	24	31	50	14	5	23	41	59
Q	29	53	33	10	4	21	46	54
R	34	12	67	15	6	20	54	46
S	30	81	6	9	4	23	40	60
	12 ^d	9 ^d	91 ^d	0	0			
T	46	96	2	1	1	7	46	54
	9 ^d	13 ^d	87 ^d	0	0			
U	51	80	17	2	<0.2	10	53	47

^a See Table III. ^b 1-Benzyloxy-2-ethylhexane. ^c Mixture of 1-benzyloxy-2-ethylhexene-3 and -4. ^d Butenyl acetates.

high molecular weight benzoates (>C₈) from the former olefin.

As shown in Table IV, the effect of copper salt on the reaction of butene-1 and benzoyl peroxide is to generate higher yields of *butenyl* benzoates, especially the crotyl isomer. In addition, two new C₈-benzoates were formed. These are isomeric 1-benzyloxy-2-ethylhexenes since they yielded 1-benzyloxy-2-ethylhexane on catalytic hydrogenation.

The copper salt concentration is more critical in these reactions than in the reactions employing butene-2, particularly with respect to the formation of octyl and octenyl benzoates. The reactions were studied in systems containing the same amount of added cuprous bromide. In hexane solvent (partially heterogeneous, lowest soluble copper salt concentration) the yields of butyl, octyl and octenyl benzoates were the highest. This was followed by the reactions in benzene (partially heterogeneous, higher copper salt concentration). The best yields of unsaturated C₄-benzoates, however, were formed in acetic acid-benzene (homogeneous). In addition, in the last solvent, butenyl acetates but no butyl acetates were formed.

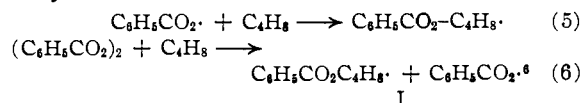
In the presence of added cupric benzoate in acetic acid-benzene and acetonitrile solvents the *butyl* benzoates were almost absent. The best yields of *butenyl* benzoates were obtained under these conditions, with minimal amounts of the saturated analogs and the C₈-benzoates. The predominant butenyl benzoate was the crotyl isomer. In acetic acid-benzene, crotyl benzoate was the sole product, while in acetonitrile it constituted 84% of the butenyl benzoate mixture. The

amount of α -methylalyl benzoate formed in the latter reaction was present in the acetic acid-benzene reaction as a mixture of butenyl acetates (predominantly α -methylalyl acetate). Under these reaction conditions the butenyl benzoates did not undergo acetolysis.

Discussion

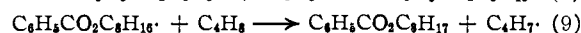
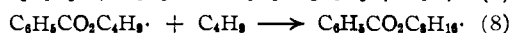
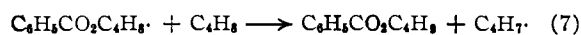
The copper salt catalyzed reaction of benzoyl peroxide and butenes differs from the reaction of *t*-butyl peresters in the formation of saturated ester products. *n*-Butyl benzoate is formed from butene-1 and *sec*-butyl benzoate from butene-2 in addition to the *butenyl* isomers, α -methylalyl and crotyl benzoates. The importance of saturated ester products is related to the concentration of the cupric salt. For example, as the solvent changed from *n*-heptane to benzene to acetonitrile and acetic acid-benzene, the yields of saturated esters among the products diminished.

In the *uncatalyzed* reaction the formation of saturated esters is postulated to occur *via* several paths, each proceeding *via* an intermediate benzyloxy-butyl radical I

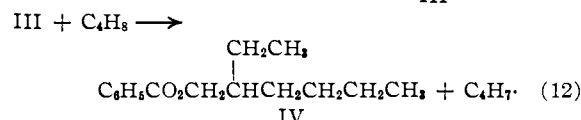
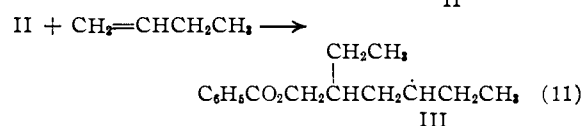
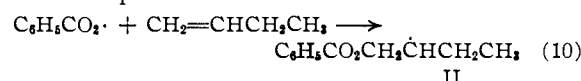


Butyl and octyl esters result from the subsequent chain transfer with butene or addition followed by chain transfer.

(6) J. C. Martin and E. H. Drew, *J. Am. Chem. Soc.*, **83**, 1233 (1961); H. J. Shine and D. Hoffman, *ibid.*, **83**, 2782 (1961); F. D. Greene, W. Adam and J. E. Cantrill, *ibid.*, **83**, 1105 (1961).



The yields of C₄-esters are determined by the relative rates of reactions 7 and 8. In this connection the lower yield of *n*-butyl benzoate from butene-1 compared to *sec*-butyl benzoate from butene-2 (compared to the formation of higher molecular weight benzoates) is in accord with the relative propensity for these terminal and internal olefins to undergo addition reactions.^{7,8} The structure of the C₈-benzoate obtained from butene-1 is consistent with the formulation given by eq. 11 and 12. Among the various octyl benzoates possible, only 1-benzyloxy-2-ethylhexane (IV) is formed. Its formation corresponds to two successive additions to the terminal position of butene-1.



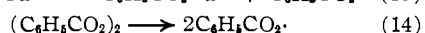
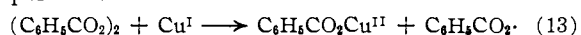
Similarly, only one octyl benzoate is formed from butene-2 and benzoyl peroxide. Its structure was not elucidated, but it is probably 2-benzyloxy-3,4-dimethylhexane.

In the *copper salt catalyzed* reaction between benzoyl peroxide and butenes, the intermediate *benzoxybutyl radicals I* also appear to be the predominant route of the reaction. Thus butene-2 yields primarily *sec*-butyl and α -methallyl benzoates with only small amounts of crotyl benzoate. Similarly, butene-1 yields primarily *n*-butyl and crotyl benzoates contaminated with only small amounts of α -methallyl benzoate.

t-Butyl perester yielded² with either butene isomer primarily the same distribution of α -methallyl ester relative to crotyl ester. The reactions were uncomplicated by the formation of *butyl* derivatives.

The benzyloxy radicals are formed by the oxidation-reduction reaction between benzoyl peroxide and cuprous ion similar to that with *t*-butyl peresters.² The production of benzyloxy radicals by (13) is only half as effective as from the purely thermolytic process (14).⁹

The extent to which processes 13 and 14 compete is a function of the cuprous concentration and temperature.¹⁰

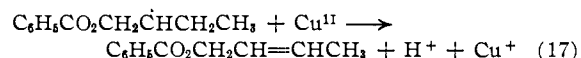
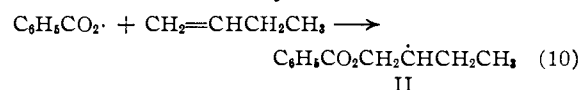
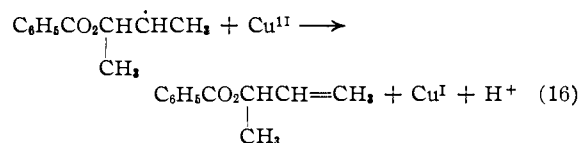
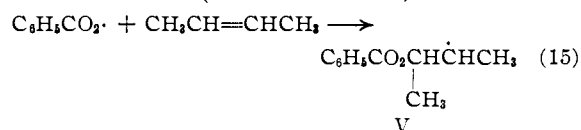


(7) The relative rates of addition (butene-1 > butene-2) is also aided slightly by the more favorable chain transfer constant (butene-2 > butene-1; J. Boland, *Quart. Revs.*, **3**, 1 (1949); A. Trotman-Dickinson and E. Steacie, *J. Chem. Phys.*, **19**, 169 (1951)).

(8) (a) M. S. Kharasch, O. Reinmuth and W. Urry, *J. Am. Chem. Soc.*, **69**, 1105 (1947); (b) E. S. Huyser, *J. Org. Chem.*, **26**, 3261 (1961).

(9) G. Hammond and L. Soffer, *J. Am. Chem. Soc.*, **72**, 4711 (1950).

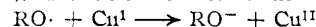
In the presence of cupric ion the benzyloxybutyl radicals are oxidized by cupric ion to form butenyl esters¹¹ by an oxidation-reduction reaction described earlier¹² (reaction 16 or 17).



The interception of the benzyloxybutyl radicals II and V must compete with the chain transfer reaction 7 and addition reaction 8. The delicate balance among the rates of all these reactions is further demonstrated by examination of the C₈-benzoate mixture. Although little (< 3%) C₈-benzoates were formed from butene-2 and benzoyl peroxide and copper salt, the more easily polymerizable butene-1 yielded among other higher molecular weight products a mixture containing these C₈-benzoates. In addition to the saturated 1-benzyloxy-2-ethylhexane there were formed two isomers which were presumed to be 1-benzyloxy-2-ethylhexene-3 (VI) and 1-benzyloxy-2-ethylhexene-4 (VII).

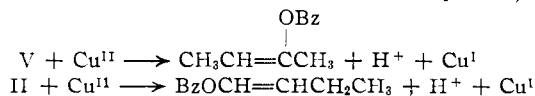
(10) The rate of the cuprous catalyzed decomposition of *t*-butyl peresters is qualitatively much faster than the rate of thermal dissociation at 80°. With di-*t*-amyl peroxide the catalyzed rate is only slightly faster than the uncatalyzed rate at 120°. Qualitatively, the copper salt catalyzed decomposition of benzoyl peroxide is similar to di-*t*-amyl peroxide in that at 75° it is only slightly faster than the uncatalyzed decomposition. These observations will be elaborated further by quantitative studies.

If the *cuprous* catalyzed reduction of certain peroxides competes with the purely thermal dissociative process than there will be a net deficit of *cupric* salts (especially in the presence of reactive hydrogen donors with which reactions 2 and 3 are rapid). In some reactions it has been observed that little cupric salt is present in the final reaction mixture.¹⁸ Under these circumstances in which relatively high steady state concentrations of both oxy radicals and cuprous salts persist, the reduction of oxy radicals by cuprous ion may be a relatively important reaction (I wish to thank Dr. Cheves Walling for this suggestion). Such electron transfer reactions



between oxy radicals and ferrous salts have been postulated previously.

(11) There are two modes by which each of the benzyloxybutyl radicals V and II can lose a β -proton. Loss of a β -proton from the benzyloxy-substituted carbon atom would result in enol ester products, e.g.

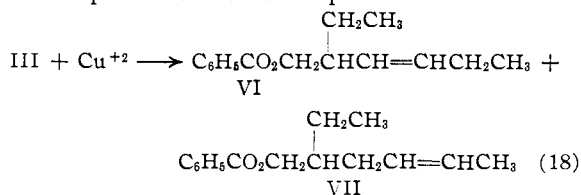


We could find little evidence for the formation of either methyl ethyl ketone or *n*-butylaldehyde from the base-catalyzed hydrolysis of the reaction products. Kharasch and Fono⁴ reported spectral evidence for the formation of some vinyl esters from octene and benzoyl peroxide. They also isolated the dinitrophenylhydrazide of octanal from the hydrolyzate of the octenyl benzoate mixture.

The selectivity observed in the oxidation of these adduct benzyloxyalkyl radicals by cupric salts to unsaturated esters will be discussed at a later time in another connection.

(12) H. De La Mare, J. Kochi and F. Rust, *J. Am. Chem. Soc.*, **83**, 2013 (1961).

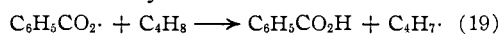
In the presence of excess cupric salt



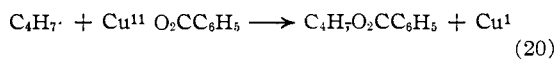
minimal amounts of these C₈-benzoates are formed. Optimum concentrations of cupric salt, therefore, must be maintained in order to avoid these (7 and 8) chain propagation reactions. However, in the case of benzoyl peroxide excessive copper concentrations will enable the catalytic decomposition of benzoyl peroxide, which is less efficient in the production of benzoxy radicals, to compete with the thermal process. The latter objection is not applicable to *t*-butyl perester reactions.

Further indication that benzoxy radicals react with butenes primarily by an addition reaction 5 is given by the relative reactivity studies on butene-2. In acetonitrile and benzene solutions *cis*-butene-2 was found to be 1.8 to 2.1 times more reactive than the *trans* isomer. These relative reactivity values are similar to those found by Skell, *et al.*,¹³ for the addition of trichloromethyl radicals to the butene-2 isomers ($k_{cis}/k_{trans} = 2.4$).

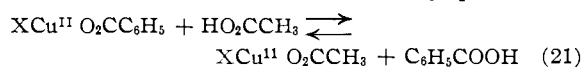
The butenyl ester products are not wholly formed *via* the cupric oxidation of the adduct benzoxybutyl radicals I. There is an alternative process involving *butenyl radicals* formed from butenes by chain transfer reactions such as 9 and 19. The formation of butenyl radicals is



followed by the oxidation-reduction reaction with cupric benzoate described earlier in the *t*-butyl perester oxidation.²



The importance of butenyl ester formation by this path is shown by the reaction of benzoyl peroxide and butene in the presence of acetic acid and acetonitrile under similar conditions. The butenyl acetates isolated in the former solvent had the same distribution of α -methallyl (87-94%) and crotyl (6-13%) isomers regardless of the reactant butene. This is in strong contradistinction to the butenyl benzoate mixture whose isomer distribution is highly dependent on the reactant olefin. This ratio of α -methallyl acetate to crotyl acetate is also the same as that obtained earlier from the *t*-butyl perester reactions. Moreover, it was shown that *t*-butyl perbenzoate reacted with butenes in acetic acid to yield predominantly butenyl acetates with minor amounts of benzoates.² This was interpreted in terms of the rapid metathesis of cupric benzoate in acetic acid solvent. The high yields of butenyl benzoates obtained from benzoyl peroxide and



butene in acetic acid solvent indicates that in these

(13) P. Skell and R. Woodworth, *J. Am. Chem. Soc.*, **77**, 4638 (1955); see, however, S. Sato and R. Cvetanovic, *ibid.*, **81**, 3224 (1959).

reactions the benzoate does not arise via the butenyl radical intermediate.

If it is assumed that all butenyl radicals formed in acetic acid yield acetates, it is possible to determine the ratio of the rates of benzoxy radical addition and hydrogen abstraction from butene. On this basis the relative rates of addition (5) to chain transfer (19) with butene-1 is calculated to be 3.6 to 1. With butene-2 it is 3.8 to 1. Similarly, by considering the difference in yield of α -methallyl benzoate formed in acetonitrile and in acetic acid-benzene the relative rates of addition to abstraction with butene-2 is 4.6 to 1.

With butene-1 it is also possible to get another indication of these relative rates from the yields of α -methallyl benzoate obtained in acetonitrile in the presence of excess cupric benzoate. Since addition of benzoxy radical to the butene-1 at the internal position is unfavored, it is assumed that most of the α -methallyl benzoate arises *via* the butenyl radical by processes 19 and 20.¹⁴ The relative rates of addition and abstraction with benzoxy radicals and butene-1 based on this assumption is 5.3 to 1. Taken all together the relative rates of addition and hydrogen abstraction of butene with benzoxy radical is approximately 4-5 to 1. These crude results cannot be used to distinguish between the reactivities of butene-1 and *cis*- or *trans*-butene-2.

These ratios of rates of addition to hydrogen abstraction in the range of 4-5 to 1, tentatively assigned for the reaction between benzoxy radical and the isomeric butenes, are not unusual. Although more sophisticated experiments are required to establish these values with greater certainty, there are indications that these ratios of rates vary considerably with structure of the free radical. Thus, Huyser^{5b} found the ratios to be 26, 34 and 43 for the reactions between the trichloromethyl radical and *cis*-butene-2, *trans*-butene-2 and octene-1, respectively. These values are in marked contrast to the low numbers obtained by Walling and Thaler^{15a} for the reaction between *t*-butoxy radicals and *cis*-butene-2 (0.20), *trans*-butene-2 (0.036) and butene-1 (0.034).^{15b}

The efficacy of cupric ion in oxidizing the benzoxybutyl radical to butenyl benzoate products can also be qualitatively interpreted as reducing the effective steady state concentration of these alkyl radicals.¹⁶ Another demonstration of these oxidation-reduction reactions between cupric ion and alkyl radicals is given by the *cis-trans* isomerization of the reactant butene. In those reactions with copper bromide catalyst, the isomerization of butene-2 is due to bromine atoms, since neither the uncatalyzed, cuprous chloride or cupric acetate catalyzed reactions induced the isomerization. In heptane and benzene solutions extensive *cis-trans* isomerization of butene-2 occurred. These were also conditions under which the least amount of butenyl esters and the greatest amount of saturated

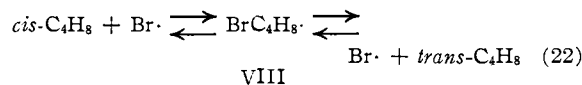
(14) This yield of α -methallyl benzoate was the same as the butenyl acetate yield in acetic acid.

(15) (a) C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961). (b) The effect of radical structure on the relative rates of addition and hydrogen abstraction reactions with olefins merits further investigation.

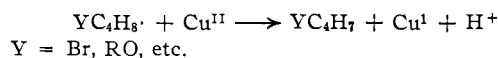
(16) Oxy radicals are unaffected by cupric ions.

and high molecular weight esters were formed. Conversely, under conditions of optimum butenyl ester formation (high cupric salt concentration) the extent of *cis-trans* isomerization was minimized (see last column, Table II).

The bromine atom catalyzed *cis-trans* isomerization of olefins is well-known.¹⁷ For butenes the mechanism is



The inhibition of the *cis-trans* isomerization by cupric ion (Table II) is due to the oxidation of the bromobutyl radical VIII, that is, in effect, removing bromine atoms from the system. The lowering of the steady state concentration of the bromoalkyl radical VIII by cupric ion thus parallels that of the benzoxybutyl radical I. We postulate that in both cases (the benzoxybutyl radical I and the bromobutyl radical VIII) cupric salt is terminating the chain reaction by an oxidation step such as



Summary

The fundamental processes in the copper salt-catalyzed reactions of *t*-butyl peresters and benzoyl peroxides with olefins thus are the same. The different product distributions obtained with each peroxide can be attributed to the initiating free radical species: *t*-butoxy radical from *t*-butyl peresters and benzoxy radicals from benzoyl peroxide. With the former the subsequent reaction path is primarily one of chain transfer by hydrogen abstraction to yield allylic radical intermediates. With benzoxy radicals, however, the addition to the olefinic bond competes with the hydrogen abstraction step (~ 5 to 1) to yield significant amounts of benzoxybutyl adduct radicals. Walling and Thaler have shown that hydrogen abstraction is the predominant route by which *t*-butoxy radicals react with butenes. Our experiments have indicated that addition is the preferred route by which benzoxy radicals react with butenes. Toward conjugated olefins, *e.g.*, butadiene and styrene, both radicals undergo facile addition to yield similar results in the copper-catalyzed reactions.¹⁸

The subsequent reactions of allylic and benzoxyalkyl radicals with cupric ions can be described in terms of one-electron oxidation-reduction steps.² Although the allylic radicals formed from abstractive processes are free to isomerize, the benzoxyalkyl radicals formed *via* addition reactions are not. Thus, butenyl benzoates formed *via* the former process are a mixture of allylic isomers.² Although there is a net shift of the double bond in the product, the butenyl benzoate formed for the addition-oxidation-elimination process is unique; butene-1 yields 1-benzoxybutene-2 and butene-2 yields 3-benzoxybutene-1 solely. In addition, the saturated butyl benzoates are formed competitively from the benzoxybutyl intermediate. The minor

amounts of 3-benzoxybutene-1 obtained from butene-1 and 1-benzoxybutene-2 from butene-2 are attributed to that part of the reaction between benzoxy radical and butene which proceeds *via* the butenyl radical formed by an abstractive process (eq. 19 and 20). By the latter route no saturated ester products are formed.

Since the products derived from the reaction of octene-1 or octene-2 with benzoyl peroxide are less amenable to characterization, Kharasch and Fono⁴ did not make unequivocal structure assignments other than to note gross structural features. The results obtained in this study are in agreement with the more qualitative results of Kharasch and Fono. The course of the reaction in both cases must proceed *via* similar paths. Thus, the predominant formation of 1-benzoxyoctene-2 from octene-1 observed by Kharasch and Fono, by the scheme outlined above, occurs *via* the oxidation of the adduct 1-benzoxy-2-octyl radical by cupric salt. The formation of smaller amounts of the isomeric 3-benzoxy-1-octene is through the oxidation of the resonance-stabilized 1-octenyl radical. Unfortunately, Kharasch and Fono did not elucidate the structures of the octenyl benzoates derived from octene-2. By analogy with the butene system, however, the predominant esters from octene-2 and benzoyl peroxide and copper salt are presumed to be 2-benzoxyoctene-3 and 3-benzoxyoctene-1. These would arise from the intermediates derived by the addition of benzoxy radical to octene-2 at either the 2- or 3-carbon atom.

Further, the routes by which alkyl and alkenyl benzenes are concomitantly formed from benzoyl peroxides and alkenes, in themselves, form an interesting problem which will be discussed at a later time.

Chart I summarizes the various routes by which ester products are formed from the reaction of benzoyl peroxide and butene-1 and butene-2 in the presence of copper salts. A similar scheme is applicable to allied olefins.

Experimental

Materials.—Cuprous bromide, Amend Drug and Chemical Co., C.P. grade; Cuprous chloride, Baker analyzed reagent; Cupric acetate, Baker analyzed reagent; Cupric benzoate, City Chemical Corp.; Benzene, Baker analyzed reagent; Acetonitrile, Matheson Co., spectroscopic grade; *t*-Butyl alcohol, Shell Chemical Co., redistilled from calcium hydride; Acetic acid, glacial, Allied Chemical reagent grade; Benzoyl peroxide, Lucidol Corp., recrystallized twice from chloroform-methanol; *cis*-Butene-2, Phillips Petroleum Co., research grade; *trans*-Butene-2, Phillips Petroleum Co., research grade; Butene-1, Matheson Co., C.P. grade; *n*-Butyl benzoate, Eastman Kodak, white label, n_D^{25} 1.4972; *sec*-Butyl benzoate, Prepared by the Schotten-Baumann procedure (b.p. 107–108° (11 mm.), n_D^{25} 1.4916); α -Methylallyl benzoate, Previously described,² n_D^{25} 1.4114; Crotyl benzoate, Previously described,² n_D^{25} 1.4240.

1-Benzoxy-2-ethylhexane.—2-Ethylhexanol-1 (Union Carbide Chemical Co.) was esterified with benzoyl chloride in pyridine. The ester produced in 85% yield distilled at 111–113° (2 mm.), n_D^{25} 1.4894.

Anal. Calcd. for C₁₅H₂₂O₂: C, 76.88; H, 9.46; ester value, 0.427. Found: C, 76.95; H, 9.41; ester value, 0.423.

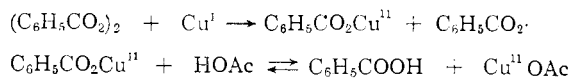
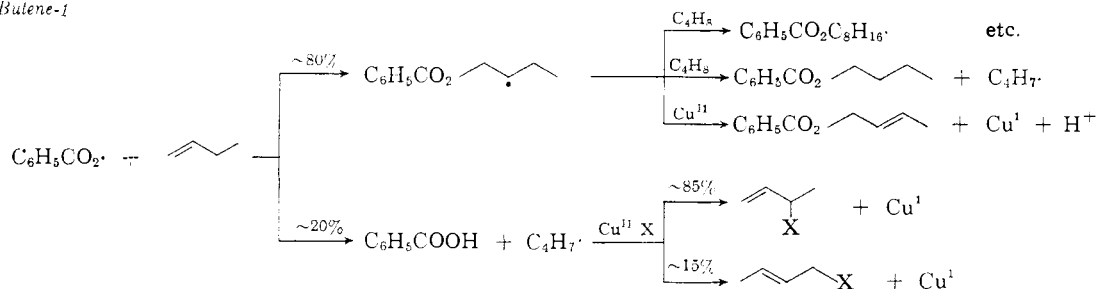
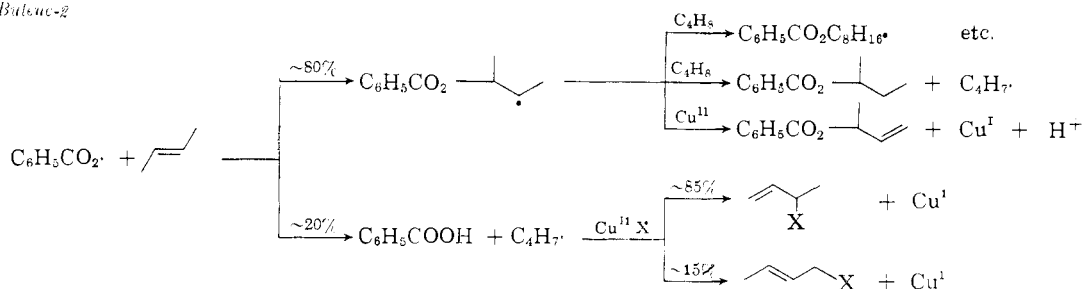
2-Benzoxybutene-2 (-1).¹⁹—A mixture of 100 g. of redistilled methyl ethyl ketone and 140 g. of benzoyl chloride

(17) C. Walling, "Free Radicals in Solution," J. Wiley and Sons, Inc., New York, N. Y., 1957, p. 302.

(18) J. Kochi, to be published.

(19) F. H. Lees, *J. Chem. Soc.*, **83**, 145 (1903); F. Young, F. Frostick, J. Sanderson and C. Hauser, *J. Am. Chem. Soc.*, **72**, 3638 (1950); W. Quattlebaum and C. Noffsinger, U. S. Patent 2,466,737.

CHART I

A. *Butene-1*B. *Butene-2*

X = CH_3CO_2 in acetic acid, otherwise $\text{C}_6\text{H}_5\text{CO}_2$

was heated at 130–135° for 32 hours under pressure (19 p.s.i.g. in excess of atmospheric). The liberated HCl was taken up in a separate stirred concentrated aqueous solution of KOH. The unreacted methyl ethyl ketone was removed under vacuum. Material boiling at 95–97° at 5 mm. was collected (51 g.); n_D^{20} 1.5139–1.5144. G.L.C. on a 10-foot Craig succinate column at 166° separated the material into 2-benzyoxybutene-2 (major component) and 2-benzyoxybutene-1 (17.9 and 23.3 minutes) in a ratio of 3:1, respectively. These structure assignments were consistent with the n.m.r. spectra.

Anal. Calcd. for $\text{C}_{11}\text{H}_{12}\text{O}_2$: C, 74.97; H, 6.86; ester value, 0.568; bromine no., 91. Found: C, 74.91, 74.69; H, 6.87, 6.88; ester value, 0.562, 0.558; bromine no., 85.

This enol benzoate did not yield a DNP derivative directly (in H_2SO_4 -ethanol). However, if it was first treated with methanolic KOH for a few minutes, methyl benzoate was immediately apparent. The mother liquors on neutralization with acetic acid and DNP reagent yielded copious amounts of methyl ethyl ketone-DNP (m.p. 113–114°). The enol benzoate mixture was hydrogenated over platinum at room temperature and 1 atmosphere pressure to yield pure *sec*-butyl benzoate.

General Procedure.—The reactions were carried out in heavy walled Pyrex vessels as described previously.² The reaction temperature was raised incrementally from 65 to 75° over a 24-hour period. The unreacted butenes were distilled from the reaction mixture and analyzed by G.L.C.² No allylic rearrangement was apparent in the recovered unreacted butenes. Except for a minor amount (~3–5%) of carbon dioxide no other volatile products were formed. An aliquot of the reaction mixture was analyzed for free carboxylic acid potentiometrically. The mixture was then washed with dilute HCl to remove copper salts, and NaHCO_3 to remove benzoic acid. The dried acid was determined gravimetrically. In acetonitrile and acetic acid solutions, *n*-pentane was first added as a diluent and the mixture then worked up. The ester solution was analyzed for total saponifiable material by the standard alkali treatment employing potentiometric techniques. The C_4 - and C_8 -esters were determined by G.L.C. on a 10-foot diethylene glycol succinate-firebrick column operated at 175° for benzoates and 90° for acetates. The relative retention times for the benzoates were: *sec*-butyl 13.8, α -methyl 15.8, *n*-butyl 27.8 and crotyl 52.2. Similar results were obtained on column utilizing Ucon polar and Craig succinate stationary phases. The acetates formed in acetic acid sol-

vents were α -methyl 10.7 and crotyl (20.4) isomers. No saturated analogs were present.

The C_8 -esters from butene-1 were determined on the Craig column at 180°: *sec*-butyl (14.8), α -methyl (17.1), *n*-butyl (22.1), crotyl (29.4), 2-ethylhexyl (68.0), 2-ethylhexenyl (70.6 and 78.1). The only C_8 -benzoate identifiable from butene-2 and benzoyl peroxide emerged at 52.2.

The C_4 - and C_8 -esters were determined quantitatively by the G.L.C. marker method.² The difference between the C_4 - C_8 esters determined in this manner and the total saponification value was attributed categorically to "higher molecular weight" esters.

The reaction mixtures were finally distilled through a 10-plate spinning band column to isolate components. C_4 -Components and C_8 -components were adequately separated by distillation. The material balance between the G.L.C. indicated yield and that obtained by distillation was 85–95% for the ester components. Those reactions which produced few isomeric products could be cleanly separated by distillation in 90–95% recovery.

The esters boiling higher than the C_4 -benzoates were only examined cursorily. The higher boiling residues from several reactions were combined and distilled *en masse*.

The mixture from butene-2 and benzoyl peroxide yielded essentially two fractions boiling range 90–103° (2 mm.) and 190–200° (2 mm.). The lower boiling fraction was a mixture of octyl and octenyl esters. *Anal.* Calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_2$: C, 77.55; H, 8.68; ester value, 0.431 equiv./100 g.; bromine no., 69. Found: C, 77.7; 77.4; H, 8.8, 8.9; ester value, 0.448, 0.450; bromine no., 49, 53. The higher boiling fraction consisted of dibenzyoxyoctanes and octenes. *Anal.* Calcd. for $\text{C}_{22}\text{H}_{26}\text{O}_4$: C, 74.55; H, 7.39; ester value, 0.565; mol. wt., 354. Found: C, 75.0, 75.1; H, 7.4, 7.3; ester value, 0.526, 0.544; bromine no. 16, 19; mol. wt. (ebullioscopic, dichloroethane) 340, 370. (Analyses given were for separate samples.) The isolated yields of these higher molecular weight esters from the catalyzed reaction varied considerably with solvent and cupric salt concentration (see Tables I and II).

The higher molecular weight esters from the reaction of butene-1 and benzoyl peroxide were also examined. The single octyl benzoate detected and isolated from the uncatalyzed reaction of butene-1 and benzoyl peroxide was 1-benzyoxy-2-ethylhexane, identical to the isomer prepared unambiguously. In the catalyzed reactions there were formed two isomeric octenyl benzoates which were not separated on distillation from the 1-benzyoxy-2-ethylhexane

(boiling range 108–115° (2 mm.)). The mixture of C₈-benzoates was hydrogenated over platinum at atmospheric pressure and room temperature quantitatively to 1-benzyloxy-2-ethylhexane. The two isomeric octenyl benzoates were formulated as: 1-benzyloxy-2-ethylhexene-3 and -4. In addition there was formed a material which analyzed for dibenzyloxyhexadecene (boiling range 200–215° (1 mm.)). *Anal.* Calcd. for C₃₀H₄₀O₄: C, 77.55; H, 8.68; ester value, 0.431; mol. wt., 464; bromine no., 34. Found: C, 77.3, 77.5; H, 8.2, 8.1; ester value, 0.424, 0.428, mole. wt., 420; bromine no., 31, 27, 38.

In addition to ester products a mixture of butyl- and butenylbenzene isomers were formed in 5–10% yields. They were not characterized. Benzene was not determined quantitatively.

The presence of 2-benzyloxybutene-2 (–1) could not be detected in the reactions of butene-2. The crude reaction

mixture was directly treated with Claisen alkali, neutralized and distilled. The distillate on treatment with DNP reagent yielded no methyl ethyl ketone-DNP. The mixture from butene-1 gave on similar treatment a small amount of propionaldehyde-DNP (m.p. 152–153°). In a similar manner, the crude reaction mixture from butene-2 and benzoyl peroxide with copper salts was distilled directly into an ice trap at atmospheric pressure to remove solvent and any material boiling less than 100°. The distillate was examined by G.L.C. (10-foot Ucon polar on Chromosorb W at 65°) but showed no methyl ethyl ketone (14.5', benzene, 18.5'). Direct examinations of the crude reaction mixture and the distilled ester reactions also gave no indication of the presence of 2-benzyloxybutene-1 or –2 (*vide supra*).

Acknowledgment.—I am indebted to Mr. Fred Rodgers for valuable technical assistance.

[CONTRIBUTION FROM THE PHYSICAL SCIENCES DIVISION, JET PROPULSION LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

A Double Resonance Study of the N.m.r. Spectrum of 1-Chlorobutadiene-1,2 and the Determination of the Relative Signs of the Coupling Constants

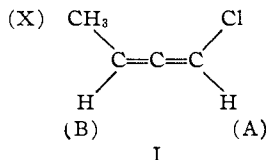
By STANLEY L. MANATT AND DANIEL D. ELLEMAN

RECEIVED OCTOBER 12, 1961

The 60 Mc. proton n.m.r. spectrum of 1-chlorobutadiene-1,2 has been studied by the audio side-band phase detection proton-proton decoupling method. Selective irradiation of certain of the spectral lines of one set of equivalent nuclei with a $\gamma H_1/2\pi$ of the order of the J 's was carried out while simultaneously recording the transitions of the other nuclei. From interpretation of the changes in the decoupled regions of the spectrum, the relative signs of J_{AB} and J_{BX} were determined to be different. Reasons why it is not possible to determine the relative signs between J_{AB} and J_{AX} by this double resonance technique are discussed. An assignment of the absolute signs with J_{BX} and J_{AX} being positive and with J_{AB} being negative has been made on the basis of the present work, the theoretical work of Karplus and the high-resolution work of Snyder and Roberts.

Introduction

From a complete analysis of the proton high-resolution n.m.r. spectra of 1-chlorobutadiene-1,2 (I) at 40 and 60 Mc., it was not possible to determine the sign of J_{AB} relative to the signs of J_{AX} and J_{BX} .¹ The present work was undertaken to see if Freeman's² double resonance technique for the determination of the relative signs of proton-proton coupling constants could be applied to the 1-chlorobutadiene-1,2 (I) molecule. The results of such experiments were expected to be of general interest in light of Karplus' recent theoretical work



on the π -electron contribution to proton-proton coupling constants.³

The first steps in applying Freeman's method for sign determination are to try to label each transition of the spectrum according to its origin in the limit as all the ratios J_{ij}/δ_{ij} approach zero (J_{ij} , coupling constant between nuclei i and j , δ_{ij} , chemical shift between nuclei i and j) and then to write down for each transition the spin states of all the neighboring nuclei which are coupled to

the nucleus responsible for that particular transition. For an ABX₃ system there is usually no question as to the assignments in the X₃ region. An approximate assignment of the origin of the lines can usually be made in the AB region even if there is some overlap of the lines of these protons. To assign the spin states of the neighboring nuclei one proceeds as follows: the first-order expression for the resonance line positions of a set of equivalent nuclei i is $\delta_i + \sum J_{ij}m_j$ where m_j is one of the possible values of the magnetic quantum number for a set of equivalent nuclei j coupled with i . The components which make up a particular m_j are the appropriate neighboring nuclear spin states. The X₃ neighboring nuclear spin states of the A proton transitions are obtained from the four possible values of m_{X_3} , $+3/2$, $+1/2$, $-1/2$ and $-3/2$ corresponding to spin states $\alpha\alpha\alpha$, $\alpha\alpha\beta$, $\alpha\beta\beta$ and $\beta\beta\beta$, respectively. The B neighboring nuclear spin states of the A proton transitions are obtained from the two possible values of m_B , $+1/2$ and $-1/2$ corresponding to spin states α and β , respectively. Thus, for each of the observed A transitions, m_B and m_{X_3} values can be assigned for a particular choice of the signs of J_{AB} and J_{AX} . Similar arguments can be used to obtain the neighboring nuclear spin states of the B and X₃ transitions.

Figures 1a and 2a show the X₃ and AB regions, respectively, of the n.m.r. spectrum of I recorded at 60 Mc. with each transition numbered. For I it is quite easy to make a complete assignment because the A and B regions do not have any overlapping lines. Thus lines 1–8 belong to nucleus

(1) E. I. Snyder and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 1582 (1962).

(2) R. Freeman and D. H. Whiffen, *Mol. Phys.*, **4**, 321 (1961); private communication from R. Freeman.

(3) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).