**Tetrahedron Letters No.30, pp. 2569–2573, 1965. Pergamon Press Ltd.
Printed in Great Britian.**

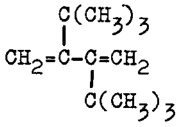
BEHAVIOR OF A NON-CONJUGATED 1,3-DIENE IN FREE RADICAL REACTIONS

Earl S. Huyser, Frederick W. Siegert and Hans Wynberg

Department of Organic Chemistry, The University, Groningen, Holland

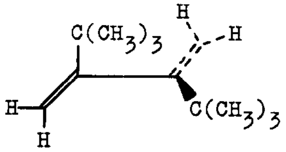
(Received 1 June 1965)

On the basis of its ultraviolet spectrum (λ_{max} 186 mμ (vapor)) and m.o. calculations, 2,3-di-t-butyl-1,3-butadiene (I) was proposed to have a skew conformation in which the



$CH_2{=}\overset{\overset{\large C(CH_3)_3}{|}}{C}{-}\underset{\underset{\large C(CH_3)_3}{|}}{C}{=}CH_2$

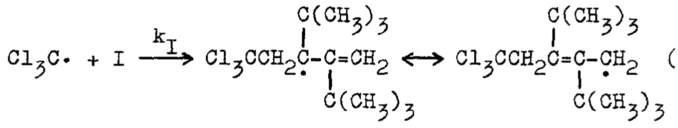
I



Ia

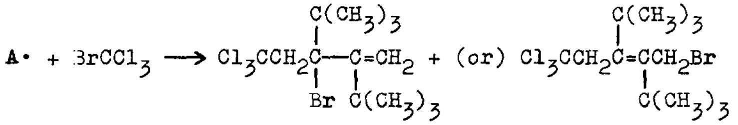
two double bonds are not in the same plane but orthogonal to each other (Ia) [1]. The prediction was made that such a 1,3-diene would not display typical behavior of a conjugated system in its reactions. We have evidence that I indeed does not react in the manner expected of a 1,3-diene in free radical reactions.

Attempts to add $BrCCl_3$ to I in both light- and benzoyl peroxide-induced reactions failed to yield any detectable amounts of either a 1,2- or a 1,4-addition product which would be expected if the reaction involved the chain sequence 1 and 2. After $3^1/_2$ hours of illumination of a mixture of $BrCCl_3$ (8.0 g., 0.04 mole) and I (1.66 g., 0.01



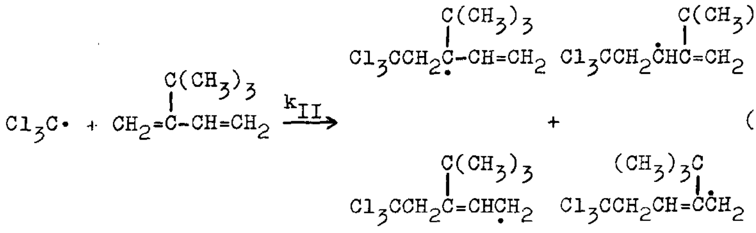
$$Cl_3C\cdot + I \xrightarrow{k_I} Cl_3CCH_2\overset{\overset{C(CH_3)_3}{|}}{\dot{C}}-\underset{\underset{C(CH_3)_3}{|}}{C}=CH_2 \longleftrightarrow Cl_3CCH_2\overset{\overset{C(CH_3)_3}{|}}{C}=\underset{\underset{C(CH_3)_3}{|}}{C}-\dot{C}H_2 \quad (1)$$

A·



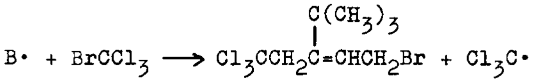
$$A\cdot + BrCCl_3 \longrightarrow Cl_3CCH_2\overset{\overset{C(CH_3)_3}{|}}{\underset{\underset{Br}{|}}{C}}-\underset{\underset{C(CH_3)_3}{|}}{C}=CH_2 + (or)\ Cl_3CCH_2\overset{\overset{C(CH_3)_3}{|}}{C}=\underset{\underset{C(CH_3)_3}{|}}{C}CH_2Br \quad (2)$$

mole) at 56°, only 5% of I had been consumed. A mixture of $BrCCl_3$ (14.8 g., 0.075 mole) and I (2.5 g., 0.015 mole) heated at 78° for 36 hours in the presence of benzoyl peroxide (0.51 g., 0.0021 mole, added in four portions during the heating period) gave a mixture from which 1.2 g. of the diene was recovered by distillation. A high boiling residue was formed but all attempts to rectify this mixture failed to yield any identifiable products other than benzoic acid. In contrast, 2-*t*-butyl-1,3-butadiene (II), a 1,3-diene reported to have properties of a conjugated system (λ_{max} 225 mμ, ε_{max} 23,240) [2] reacted readily with $BrCCl_3$. Two hours of illumination of a mixture of $BrCCl_3$ (8.8 g., 0.044 mole) and II (2.5 g., 0.022 mole) yielded 2.5 g. (36% of theory) of the 1,4-addition products III and IV.[3]



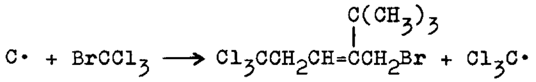
$$Cl_3C\cdot + CH_2=\overset{\overset{C(CH_3)_3}{|}}{C}-CH=CH_2 \xrightarrow{k_{II}} \begin{matrix} Cl_3CCH_2\overset{\overset{C(CH_3)_3}{|}}{\dot{C}}-CH=CH_2 & Cl_3CCH_2\dot{C}H\overset{\overset{C(CH_3)_3}{|}}{C}=CH_2 \\ + & \\ Cl_3CCH_2\overset{\overset{C(CH_3)_3}{|}}{C}=CH\dot{C}H_2 & Cl_3CCH_2CH=\overset{\overset{(CH_3)_3C}{|}}{\dot{C}}H_2 \end{matrix} \quad (3)$$

B· C·



$$B\cdot + BrCCl_3 \longrightarrow Cl_3CCH_2\overset{C(CH_3)_3}{\overset{|}{C}}=CHCH_2Br + Cl_3C\cdot \qquad (4)$$

III



$$C\cdot + BrCCl_3 \longrightarrow Cl_3CCH_2CH=\overset{C(CH_3)_3}{\overset{|}{C}}CH_2Br + Cl_3C\cdot \qquad (5)$$

IV

The relative reactivities toward addition of $Cl_3C\cdot$ of I and II with respect to 1-octene, an alkene that readily undergoes addition $BrCCl_3$ via the chain sequence 6 and 7, were determined by competition reactions of each diene with 1-octene toward addition of $BrCCl_3$.[4]

$$Cl_3C\cdot + CH_2=CHC_6H_{13}\text{-}\underline{n} \xrightarrow{k_o} \underset{D\cdot}{Cl_3CCH_2\dot{C}HC_6H_{13}\text{-}\underline{n}} \qquad (6)$$

$$D\cdot + BrCCl_3 \longrightarrow Cl_3CCH_2CHBrC_6H_{13}\text{-}\underline{n} + Cl_3C\cdot \qquad (7)$$

TABLE I

Relative reactivities of I and II with respect to 1-octene toward addition of $Cl_3C\cdot$ at 56°

Reactivity ratio	Value	No. of runs	Average deviation
k_I/k_o	0.26	3	0.03
k_{II}/k_o	62	4	11

The high reactivity of II with respect to 1-octene toward addition of $Cl_3C\cdot$ is typical of a truly conjugated diene. The comparatively low reactivity of I supports the hypothesis[1] that no conjugative effect would be encountered in reaction of this diene.

We found that I does not copolymerize with styrene. This is also indicative of a very low reactivity of this diene in radical addition reactions. The polymer obtained from heating I with styrene in the presence of benzoyl peroxide had an n.m.r. and infrared spectra indistinguishable from that of pure polystyrene. On the other hand, II copolymerized readily with styrene as would be expected for a normal conjugated diene.[5]

Although the reactivity of I toward addition by $Cl_3C\cdot$ is low compared to a truly conjugated 1,3-diene, its reactivity in this reaction is comparable to that of 1-octene which does form addition products with $BrCCl_3$. Finding no addition products in the reactions of I with $BrCCl_3$ suggests that the reaction of the adduct radical A· with $BrCCl_3$ (reaction 2) is the limiting factor in the chain sequence 1 and 2. Attack of the hybrid radical A· at either the 2-carbon or the 4-carbon may be hindered by the two _t_-butyl groups. The residue formed in the benzoyl peroxide-induced reaction of I with $BrCCl_3$ quite possibly is a mixture of products resulting from termination reactions (possibly coupling but more likely disproportionation) of the adduct radicals.

Support for the suggestion that reaction 2 is the limiting factor in the chain sequence 1 and 2 can be found in the inhibitory effect that I has on the reaction of 1-octene with $BrCCl_3$. Whereas 20 mole percent 1-octene in $BrCCl_3$ was almost completely consumed in 15 minutes in a light-induced reaction at 56°, the presence of 10 mole percent of I in the reaction mixture reduced the half-life of 1-octene to 80 minutes under identical conditions. Reaction of $Cl_3C\cdot$ with I to yield the unreactive radical A· would shorten the normally long kinetic chain length of the reaction of 1-octene with $BrCCl_3$.

A more complete report on the behavior of I and II in free radical reactions will be made elsewhere.

Acknowledgment: We wish to thank Mr.H. Sinnige for technical assistance and one of us (E.S.H.) wishes to acknowledge his support by the National Science Foundation in the form of a Senior Postdoctoral Fellowship during the course of this investigation.

REFERENCES

1. H. Wynberg, A. De Groot and D.W. Davies, Tetrahedron Letters, No. 17, 1083 (1963).
2. C.G. Overberger, A. Fischman, C.W. Roberts, L.H. Arond and J. Lal, J. Am. Chem. Soc., 73, 2540 (1951).
3. B.p. 60° at 0.1 mm., n_D^{20} 1.5203. No infrared absorption in the terminal methylene absorption region of 855-995 cm^{-1}. The n.m.r. spectrum showed two singlets at 1.18 and 1.22 p.p.m. due to two t-butyl groups as well as resonance peaks in the 3.4 to 4.4 p.p.m. region due to the methylene groups and from 5.6 to 6.3 due to vinyl protons. The integrated areas were consistent with 1,4-addition products (9:4:1 respectively).
4. F.R. Mayo and C. Walling, Chem. Rev., 46, 191 (1950).
5. M.S. Kharasch, O. Reinmuth and W.H. Urry, J. Am. Chem. Soc., 69, 1105 (1947).