systems at liquid air temperatures.[7,15] Production of H_2 at such low temperatures[16] suggests that

$$H + H \longrightarrow H_2 \qquad (7)$$

H atoms may find each other with high probability even at liquid air temperature.

In order to understand the decrease in H_2 yield at intermediate temperatures, we assume that the probability of some reaction of low activation energy, *e.g.*, addition of H atom to a double bond (*cf.* the drops in isobutylene yield and corresponding rise in isobutane at such temperature), increases with temperature. Were there no compensatory process, the effect of increased temperature would be to reduce $G(H_2)$ to a value approximating the yield in the presence of iodine scavenger.[11]

As the temperature rises, a new source of H_2, the reaction

$$H + C_5H_{12} \longrightarrow H_2 + C_5H_{11} \qquad (8)$$

which has an activation energy of *ca.* 9.2 kcal.,[14b] becomes increasingly important so that H_2 yield tends to increase, as found.

Critique of Suggested Mechanism.—The mechanism outlined in the preceding section is consistent with, or accounts for, the results and the findings outlined in the section entitled Requirements of a Mechanism with the notable exception that we have offered no detailed suggestions as to mechanism of formation of intermediate hydrocarbons. Furthermore, possible contribution of ionic reactions, *e.g.*, of the interesting type possible in liquids[17]

$$M^{+}{\cdot}M + e \rightarrow \text{products} \qquad (9)$$

is completely ignored. Reactions of type 9 may be particularly important at low temperatures and might account both for increased $G(H_2)$ and for increased $G(C_8)$, $G(C_9)$ and $G(C_{10})$ under such conditions. It is interesting to note in connection with such a proposed process 9 that iodine has no effect on $G(\Sigma C_4)$, *i.e.*, G of total C_4 products, or on G (neohexane) and that $G(\Sigma C_4)$ is approximately the same as G (neohexane) at all temperatures.

Acknowledgments.—The authors are greatly indebted to Professor G. F. Hennion who provided both the material and the technique for synthesis of authentic dineopentyl and to Mr. C. A. Lynch who actually synthesized it.

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[15] R. Livingston, H. Zelder and E. H. Taylor, *Discussions Faraday Soc.*, **19**, 166 (1955); N. J. Cherniak, *et al.*, *Doklady Akad. Nauk S.S.S.R.*, **120**, 346 (1958); *cf.*, however, F. S. Dainton, *Discussions Faraday Soc.*, **19**, 183 (1955).

[16] R. L. Livingston, *Radiation Research Supplement*, **1**, 463 (1959), and forthcoming publication, notes a correspondence between sensitivities to solute of G(H), as established by paramagnetic resonance studies on irradiated ice and of $G(H_2)$ obtained after melting.

[17] M. Burton, *J. Chem. Ed.*, **36**, 273 (1959).

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Relation Between Methyl Affinities and Conformation of the Conjugated Dienes

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Received May 3, 1960

Methyl affinities of 1,2-dimethylenecyclobutane, 1,2-dimethylene-3-methylcyclopentane and 1,2-dimethylenecyclohexane were determined. The first two dienes were shown to be 2.3 and 3.2 times as reactive as butadiene or isoprene, whereas the last compound is only one-half as reactive as butadiene. The relatively low reactivity of the latter compound is explained by the lack of coplanarity of its vinyl groups. On the other hand, the unusually high reactivity of the first two compounds calls for a new hypothesis. It is suggested tentatively that the co-planar *cis*-conformation of the vinyl groups introduces considerable steric strain which is released in the transition state as a result of the change from the sp_2 to sp_3 configurations. This may lower the activation energy of the process and increase the respective methyl affinity. Moreover, such an explanation accounts for the higher reactivity of the cyclopentane derivative than that of the cyclobutane derivative since the reactive CH_2 centers are more closely placed in the former compound than in the latter.

Kinetic studies of the addition of methyl radicals to butadiene-1,3, isoprene and 2,3-dimethylbutadiene demonstrated a very close similarity in the reactivities of these hydrocarbons[1,2] (see Table I). The observed methyl affinities, *i.e.*, the relative rate constants of methyl radical addition, can be actually accounted for quantitatively by considering the localization energy of butadiene and the effects of hyperconjugation.[3,4]

Conjugated dienes may exist in two conformations, namely a *cis* conformation in which both vinyl groups are located on the same side of the C–C bond, and the *trans* one with the vinyl groups located on the opposite sides of this bond. Spectroscopic studies of butadiene[5] showed that the *trans* conformation is preferred for this hydrocarbon and the difference in energy levels of the *cis*- and *trans*-conformations was estimated to be 2.3 kcal./mole. Hence, in the equilibrium established at 65° more than 97% of that compound is present in the *trans* rotational form. On the other hand, recent spectroscopic studies of Nikitin and Yakovleva[6] lead them to conclude that the preferred conformation of isoprene is *cis*, which means that the latter rotational isomer forms at 65° the bulk of this hydrocarbon.

If the assignments of these conformations are correct, then the kinetic results, mentioned at the

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[1] A. Rajbenbach and M. Szwarc, This Journal, **79**, 6343 (1957).

[2] A. Rajbenbach and M. Szwarc, *Proc. Roy. Soc.* (*London*), **A251**, 1266 (1959).

[3] M. Szwarc and J. H. Binks, "Theoretical Organic Chemistry, Kekule Symposium, 1958," Butterworth, 1959.

[4] J. H. Binks and M. Szwarc, *J. Chem. Phys.*, **30**, 1494 (1959).

[5] J. G. Aston, G. Szasz, H. W. Wooley and F. G. Brickwedde, *ibid.*, **14**, 67 (1946).

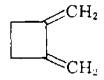
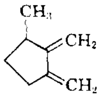
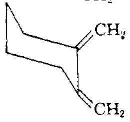
[6] V. N. Nikitin and T. V. Yakovleva, *Zhur. Fiz. Khem.*, **28**, 697 (1954).

beginning of this paper, would indicate that the addition of methyl radicals proceeds equally rapidly with the *cis*- and the *trans*-rotational isomer of the conjugated diene. This problem was now examined further by investigating the rates of methyl radical addition to 1,2-dimethylenecyclobutane, 1,2-dimethylene-3-methylcyclopentane and 1,2-dimethylenecyclohexane. The Experimental Results, summarized in Table I, show clearly that the reactivities of the first two compounds are considerably greater than the reactivity of butadiene or isoprene (the respective values are larger by factors of about 2.3 and 3.3 than those of the linear dienes) while the reactivity of 1,2-dimethylenecyclohexane is only one-half of that of butadiene. These results led us to reconsider the relation between the reactivities of conjugated dienes and their conformations.

TABLE I

METHYL AFFINITIES (RELATIVE RATE CONSTANTS OF METHYL RADICALS ADDITION) OF CONJUGATED DIENES

Solvent–iso-octane; $T = 65°$

Conjugated diene	k_2/k_1 = methyl affinity[a]
Butadiene-1,3	2015 ± 30 (ref. 1,2)
Isoprene	2090 ± 50 (ref. 1,2)
2,3-Dimethyl butadiene	2230 ± 70 (ref. 1,2)
	4750 ± 35
	6575 ± 110
	1015 ± 55

[a] k_I – rate constant of CH_3 + iso-octane → CH_4 + iso-octyl radical. k_2 – rate constant of CH_3 + diene → $CH_3 \cdot$diene.

Experimental

1,2-Dimethylenecyclobutane was kindly provided by Dr. V. A. Engelhardt of Du Pont Co. The sample was a mixture of 85% of pure 1,2 isomer and 15% of pure 1,3 isomer. Its reactivity was determined without separating the isomers and the results were then recalculated to give the proper value for the pure 1,2 isomer. The necessary correction factor was obtained from the independently determined methyl affinity of pure 1,3-dimethylenecyclobutane, a sample of which was also provided by Du Pont Co. The latter compound was found to be about 35 times less reactive than the 1,2, isomer.

1,2-Dimethylene-3-methylcyclopentane was prepared by the method of Blomquist.[7] The purity of the final, carefully distilled product was tested by gas-chromatography and only one peak was observed.

A sample of 1,2-dimethylenecyclohexane was obtained from Dr. W. A. Henderson of Yale University, and a gas-chromatographic analysis suggests that it was a pure compound.

Methyl affinities of all the investigated hydrocarbons were determined at 65° in iso-octane solution. The details of the experimental technique are given in reference 2. The results and conditions of individual experiments are summarized in Table II.

Discussion

Before proceeding with the discussion of our results let us consider first of all the geometry of the investigated compounds. Assuming that the length of single C–C and double C=C bonds in 1,2-dimethylenecyclobutane and 1,2-dimethylene-3-methylcyclopentane are the same as in butadiene-1,3, *i.e.*, 1.46 and 1.35 Å. respectively,[8] and that the length of the C–H bonds is 1.06 Å., we calculated the distances between the hydrogen atoms on the methylene carbons of the respective vinyl groups. The results are given in Table III, and in the calculations it was assumed that all these molecules are planar and that the angle between the vinyl groups is 90° in the cyclobutane derivative, 72° in the cyclopentane derivative and 60° in the *cis*-conformation of butadiene-1,3.

TABLE II

METHYL AFFINITIES DETERMINED IN ISO-OCTANE SOLUTION AT 65° CONCENTRATION OF ACETYL PEROXIDE 1–3 × 10^{-3} *M*

Investigated diene	Conc., mole %	k_2/k_1
1,2-Dimethylenecyclobutane (85% + 15% 1,2-)	0.0352	4070
1,2-Dimethylenecyclobutane (85% + 15% 1,2-)	.0470	4060
1,2-Dimethylenecyclobutane (85% + 15% 1,2-)	.0940	4250
1,2-Dimethylenecyclobutane (85% + 15% 1,2-)	.141	4020
1,2-Dimethylenecyclobutane (85% + 15% 1,2-)	.164	3905
	Av.	4060 ± 25
	Corr. av.	4750 ± 35
1,2-Dimethylene-3-methylcyclopentane	0.0253	6960
1,2-Dimethylene-3-methylcyclopentane	.0506	6690
1,2-Dimethylene-3-methylcyclopentane	.0674	6250
1,2-Dimethylene-3-methylcyclopentane	.0843	6700
1,2-Dimethylene-3-methylcyclopentane	.118	6280
	Av.	6575 ± 110
1,2-Dimethylenecyclohexane	0.10	1000
1,2-Dimethylenecyclohexane	.12	1072
1,2-Dimethylenecyclohexane	.15	1071
1,2-Dimethylenecyclohexane	.15	1060
1,2-Dimethylenecyclohexane	.20	986
1,2-Dimethylenecyclohexane	.25	1012
1,2-Dimethylenecyclohexane	.30	907
	Av.	1015 ± 55

Inspection of Table III shows that the distance between the vinyl groups of the cyclopentane derivative is smaller than that in the cyclobutane derivative. Indeed, in the latter compound the hydrogen atoms are comfortably distant, in the former derivative they repel each other to some degree, whereas a considerable strain is developed in the *cis*-conformation of butadiene.

TABLE III

Derivative of	Angle between vinyl groups	Distance between CH_2's of vinyl groups, Å.	Distance between H's of vinyl CH_2's, Å.
Cyclobutane	90	3.3	2.75
Cyclopentane	72	3.0	2.05
cis-Conformation of butadiene-1,3	60	2.75	1.70

Examination of the model of 1,2-dimethylenecyclohexane indicates that in this compound the vinyl groups are not co-planar. This conclusion is supported further by the ultraviolet absorption studies. The compound absorbs at 2200 Å. according to Bailey[9] or at 2220 Å. according to Blomquist[10] with an extinction coefficient ϵ = 3.6–3.82, whereas the absorption of dimethylenecyclopen-

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[7] A. T. Blomquist, J. Wolinsky, Y. C. Meinwald and D. T. Longone, THIS JOURNAL, **78**, 6057 (1956).

[8] "Tables of Interatomic Distances," Edited by L. E. Sutton, Spec. Public. Chem. Soc. No. 11 (1958).

[9] W. J. Bailey and H. R. Golden, THIS JOURNAL, **75**, 4780 (1953).

[10] T. A. Blomquist and D. T. Longone, *ibid.*, **79**, 3916 (1957).

tane takes place at 2480 Å. with an extinction coefficient $\epsilon = 4.02$.[10] It is probable that the vinyl groups are inclined by about 60° to each other, and if the change in localization energy with the angle of inclination is given approximately by a cosine function, one expects the reactivity of 1,2-dimethylenecyclohexane to be about one half of that of butadiene. This indeed is the case.

The experimental data suggest, therefore, that the high reactivities of 1,2-dimethylenecyclobutane and 1,2-dimethylene-3-methylcyclopentane are associated with their coplanar *cis*-conformation. At the same time, it appears that the deformation of the sp^2 valence angles, which occurs in these compounds, does not affect their methyl affinities. Although this deformation is relatively small in the cyclopentane derivative, its methyl affinity is *higher* than that of the cyclobutane derivative in which the sp^2 angle deformation is substantially larger. Moreover, the methyl affinity of methylenecyclobutane was measured,[11] and its was found to be only 42.5, *i.e.*, insignificantly higher than the methyl affinity of isobutene (a value of 36 for the latter compound was reported by Buckley and Szwarc[12]).

To explain all these results, we propose tentatively that the high values of methyl affinities arise from the release of the steric strain in the transition state which exists in the initial state as a result of the too close proximity of the non-ring CH_2 groups. The change of the configuration around the reactive carbon atom from sp_2 to a configuration approaching that of sp_3 lowers the activation energy of the process. Moreover, if the proposed transition state correctly describes the course of the addition, then a higher methyl affinity is expected for that compound in which the reactive CH_2 centers are closer together. This again is the case, since the reactivity of the cyclopentane derivative (the CH_2 groups placed at a distance of 3.0 Å.) is substantially greater than the reactivity of cyclobutane derivative where the respective distance is 3.3 Å.

In view of this discussion we have to dispute the conformation of isoprene proposed by Nikitin and Yakovleva.[6] Examination of the models reveals enormous repulsion between the non-bonded hydrogen atoms of the vinyl groups if placed in a *cis*-conformation (see Table III). Actually, using Kreevoy's[13] potential energy function for the interaction between non-bonded hydrogen atom, we calculate the strain energy in the *cis*-conformation of isoprene, with the methyl group eclipsed in respect to the other vinyl group, to be substantially more than 12 kcal./mole, while the strain energy of the *trans*-conformation is only 9 kcal./mole (the methyl group eclipsed again in respect to the other vinyl group[14]). These calculations provide a powerful argument against the conformation proposed by Nikitin and Yakovleva. Moreover, the close values for methyl affinities of butadiene, isoprene and 2,3-dimethylbutadiene suggest the same *trans*-conformation for all these hydrocarbons.

The skewed conformation of isoprene and 2,3-dimethylbutadiene should diminish substantially the strain energy resulting from the interaction between the non-bonded atoms. However, values for their methyl affinities leave no doubt that these hydrocarbons are co-planar. This shows the importance of conjugation in establishing the conformation of the molecule.

In conclusion, we would like to thank Dr. V. A. Engelhardt and Dr. W. A. Henderson for their help in acquiring the investigated compounds. We gratefully acknowledge the financial support of this investigation by The National Science Foundation.

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(11) Unpublished results from our Laboratory.

(12) R. P. Buckley and M. Szwarc, *Proc. Roy. Soc.* (*London*), **A240**, 396 (1957).

(13) E. A. Mason and M. M. Kreevoy, THIS JOURNAL, **77**, 5805 (1955).

(14) The strain energy is by about 1 kcal./mole greater if the methyl group is eclipsed in respect to the adjacent H atom of the same vinyl group.