Action of Di-*tert*-butyl Peroxide or of γ-Radiations on 2,3-Dimethylbutane. Identification of the C_{12} Hydrocarbons

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The reaction between 2,3-dimethylbutane and di-*tert*-butyl peroxide might lead in principle to 21 saturated and unsaturated products. Capillary GLC reveals six major compounds which have been isolated by fractional preparative GLC and whose structure has been for the first time unambiguously determined by spectroscopy (^{1}H NMR, ^{13}C NMR, mass), independent synthesis, hydrogenation of reaction mixtures, and chromatographic retention data. These three last techniques permit also the plausible identification of ten other products present in lower concentrations and which were not separated from the reaction mixture. This study points also out that the dehydrodimerization of tertiary alkanes is not an interesting method for the synthesis of unsubstituted vicinal biquaternary hydrocarbons as erroneously suggested by Meshcheryakov and Erzyutova. It permits, however, a better understanding of the behavior of the intermediate alkyl and allyl radicals and emphasizes the particular physical properties of the vicinal biquaternary alkanes.

The dimerization of carbon-centered radicals has been much investigated. The dimerizing radicals are generally generated by the action of a peroxide on the corresponding alkane and the reaction is then called a dehydrodimerization:[2]

$$\text{peroxide} \xrightarrow[\text{light}]{\text{heat or}} 2\text{Q}\cdot \tag{1}$$

$$\text{Q}\cdot + \text{RH} \rightarrow \text{QH} + \text{R}\cdot \tag{2}$$

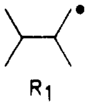
$$2\text{R}\cdot \rightarrow \text{R–R} \tag{3}$$

The R· radicals which lead to the formation of the R–R dimers are stabilized by substituents like phenyl, cyano, halogens, carbonyl, etc. A few studies deal with unsubstituted alkanes[2] but the nature of the reaction products is generally not determined. Meshcheryakov and Erzyutova, however, claim that the dehydrodimerization of 2-methylbutane, 2,2,4-trimethylpentane, and 3-ethylpentane leads in each case to the formation of the biquaternary dehydro dimer. However, in order to prove the structure of these compounds they mention only boiling points, refractive indexes, densities, and elemental analysis.[3]

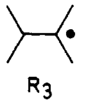
We have reinvestigated the action of di-*tert*-butyl peroxide (DTBP) on 2-methylbutane and on 2,2,4-trimethylpentane. In both cases, the reaction mixture is quite complex as seen by capillary GLC.[4]

On the other hand, the γ-radiolysis of simple alkanes has been extensively studied. In these reactions different mechanisms are operative but in certain cases the radical one prevails to a large extent. Unfortunately, the exact nature of the reaction products is generally not determined.

In this paper we present the determination of the C_{12} products obtained by the action of di-*tert*-butyl peroxide (DTBP) or of γ-radiations on 2,3-dimethylbutane (2,3-DMB).

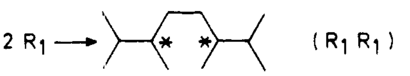


R_1

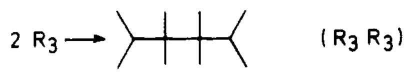


R_3

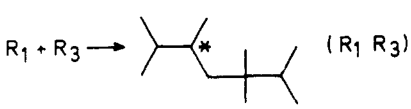
This compound gives primary (R_1) and tertiary (R_3) radicals. The former is statistically favored. The latter is, however, more stable ($R_{\text{tert}} > R_{\text{sec}} > R_{\text{prim}}$). For the coupling of these radicals three routes are possible:



(4)



(5)



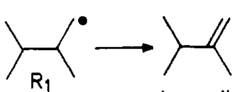
(6)

The R_1R_1 dimer has two asymmetric carbon atoms; therefore, the meso and racemic forms must be formed but may or may not be separated by GLC.[5]

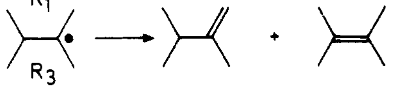
Radicals are also able to disproportionate into alkane and alkene:

$$2\text{R}\cdot \rightarrow \text{R}(+\text{H}) + \text{R}(-\text{H}) \tag{7}$$

R_1 gives only the 1-butene, R_3 the 1- and 2-butenes:

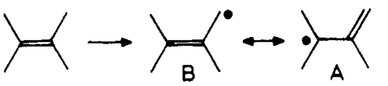


(8)

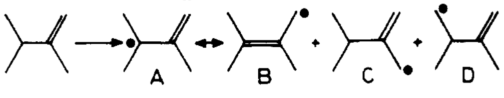


(9)

These alkenes are more reactive than the corresponding alkanes and, although in lower concentrations, will therefore intervene in the reaction:



(10)



(11)

Radical D, being nonallylic, is less probable than radicals A ↔ B and C. The tendency to disproportionate (k_d) and to combine (k_c) is not the same for all radicals. For tertiary radicals $k_d \simeq 5k_c$, for secondary ones $k_d \simeq k_c$, and for primary ones $k_d \simeq \frac{1}{6}k_c$. For resonance-stabilized radicals k_d/k_c is very low.[2]

Thus from the A ↔ B, C, D, R_1, and R_3 radicals, 21 compounds are possible: three alkanes, eight monoalkenes, and ten nonconjugated dienes. Castello, Munari, and Grandi observed only three major peaks in the C_{12} range during γ-radiolysis of 2,3-DMB.[6-8] These authors attributed them to R_3R_3, R_1R_3, and R_1R_1, respectively, but did not give a precise description of their identification method.[9]

Other reactions may not in principle be rejected: for example, the combination of alkyl and alkoxyl radicals or the addition of radicals to an olefin. Such reactions may perhaps

Table I. Retention Times and GC Area Percentages for the C_{12} Hydrocarbons Obtained by Action of DTBP or of γ-Radiations on 2,3-DMB

		GC area percentages				
		Peroxide reaction		γ-Radiolysis[20]		
Peak	Retention times, min[a]	UV (35 °C)	137 °C	Solid I[b]	Solid II[c]	Liquid[d]
2/3	31.9/32.2	2.3	11.6	4.1	1.7	8
4	32.9	32.8	17.1	15.3	6.6	8
5	33.9	1.8	1.2			
6	34.4	13.7	24.1	18.6	17.9	31
7	34.9	2.0	1.8	3.3	4.0	17
8/9	35.9/36.3	3.8	9.9	40.1	65.0	22
13	43.5	0.4	0.3	5.0	3.5	2
14	44.5	12.5	8.9	11.1	0.3	6
15	46.5	4.8	2.5			Tr
17	52.0	25.9	22.7	2.5	0.9	6

[a] For the GC analysis conditions, see Experimental Section. [b] Transparent glass. [c] Opaque solid after annealing. [d] At room temperature.

account for small quantities of products which elute before the C_{12} hydrocarbons. The yields of these products are, however, not important. This is not surprising since the disproportionation/combination ratio is much higher for alkyl/alkoxyl radical pairs than for alkyl/alkyl radical pairs.[10] On the other hand, alkoxyl radicals tend to abstract allylic hydrogen atoms much more than to add to double bonds.[11-13] At room temperature *tert*-butoxyl radicals are stable and give almost exclusively *tert*-butyl alcohol. At higher temperatures *tert*-butyl alcohol and acetone are obtained but the yields of the products eluting between them and the C_{12} hydrocarbons increase only slightly.[14] Actually, methyl radicals do not tend very much to add to crowded olefins. The "blocking effect" of methyl groups has been discussed by Szwarc.[16] Methyl radicals probably have more tendency to dimerize, to abstract hydrogen atoms, or eventually to combine with other radicals. The addition to olefins of more complex alkyl radicals has only scarcely been mentioned in the course of such reactions. Ipatieff has explained by such a mechanism the presence of 2-methyl-2,4-di-*p*-tolylpentane in the oxidation of *p*-cymene.[17]

Experimental Section

Analyses of the reaction mixtures were performed on a Varian 1440 chromatograph equipped with a glass capillary column (85 m × 0.5 mm) of silicone OV-1 and with a variable splitter adjusted to a 1:10 ratio. The flow of the nitrogen gas in the column was 3.8 mL/min. The temperatures of the column, the injector, and the detector were 92, 122, and 205 °C, respectively. Under these conditions the retention times of the C_{12} products range between 32 and 52 min (Table I). Under the same conditions the air peak appears after 9.5 min, *n*-decane elutes after 23.5 min, 2-methyldecane after 30.7 min (just after peak 1), *n*-undecane after 35.9 min (together with peak 8), and *n*-dodecane after 58.8 min. The separation of the products was achieved on a Varian 711 chromatograph equipped with aluminum columns (7 m × 0.375 in.) of silicone SE-30 (injector/detector 225 °C; column 140 °C; nitrogen 300 mL/min).

The ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer, the ^{1}H NMR spectra on Varian XL-100 or EM-360 spectrometers. The mass spectra were taken on a Varian MAT 311 system.

The hydrogenation reactions were conducted at 70 °C in a 40-mL Pyrex vessel containing 200 μL of the olefin, 12 mL of cyclohexane, and 2 g of Raney nickel. The reactor was flushed by nitrogen and then by hydrogen. At the beginning of the reaction the hydrogen overpressure was 1 kg/cm^2. The reactor was vigorously shaken during the experiment which, for tetrasubstituted olefins, took about 20 h.

Boiling temperatures were automatically recorded on a Mettler FP 1 apparatus.

2,3-DMB (Koch-Light product) and DTBP (Fluka product) were irradiated by UV light (Q 300 original Hanau HP mercury lamp) in quartz tubes at 35 °C.[18] In other experiments the peroxide was thermally decomposed at 137 °C in Pyrex sealed tubes.[19] In both cases the reaction time was adjusted so that the major part of the peroxide (90–95%) was decomposed (approximately 32 and 16 h). The molar hydrocarbon/peroxide ratio was quite high (10:1) in order to avoid induced decomposition of the peroxide and also consecutive reactions leading to the formation of higher molecular weight material. After analysis of the C_{12} hydrocarbons the temperature of the GLC column was raised from 92 °C to 195 °C and maintained so for 1 h; only a limited amount of such material was found which was estimated to be 10–20% of the C_{12} fraction. Furthermore, chromatographic analysis of the reaction mixture at different times during the reaction showed that the relative percentages of the different peaks remain almost constant.

Results and Discussion

The chromatographic data (GLC retention times and area percentages) for the C_{12} compounds obtained during decomposition of DTBP in 2,3-DMB are given in Table I. In the γ-radiolysis of 2,3-DMB at 77 K,[20] the same products have been obtained except those corresponding to peaks **5** and **15**. In the liquid phase at room temperature only peak **5** is missing. In the peroxide reaction few compounds are found on the gas chromatograms between the light compounds (2,3-DMB, *tert*-butyl alcohol, acetone, etc., eluting just after the air peak) and the C_{12} fraction. This is, however, not the case in the γ-radiolysis, especially in the liquid phase at room temperature.[6,20]

After irradiation, the C_{12} compounds are separated from the light and heavy products by fractional distillation at 16 mmHg pressure ($\simeq$85 °C). The preparative chromatographic separation is quite poor on packed columns and for large amounts of products. Although compounds **4–9**, for example, reveal only one peak, samples collected at the beginning or at the end of the signal show slightly different compositions. It is therefore possible to obtain enriched fractions for the different products. By reinjecting these fractions ("fractional preparative GLC") the purity level may become high enough to permit their identification (Table II).

Mass Spectrometric Analysis. The mass spectra of the different samples do not yield much information about the structure of the compounds. Even at low excitation potentials, the molecular peak of such branched compounds is generally absent or very weak. Fraction C, however, reveals a weak peak at *m/e* 170, and fractions A, D, and E a weak peak at *m/e* 168. Therefore, it is likely that peaks **8/9** correspond to aliphatic dimers, probably R_1R_1, since this compound exists as a meso/racemic mixture and is more stable than the other two dimers. Furthermore, peaks **4**, **14**, and **15** must correspond to monoolefinic products. For alkanes, the major peaks are located at *m/e* 85, 71, 57, 43, and 29; for olefins, the peaks at *m/e* 83, 69, 55, 41, and 27 are appreciably increased. On this basis, compounds **6**, **8/9**, and **17** are alkanes and the olefinic nature of **4**, **14**, and **15** is confirmed. Sample E revealing also a peak

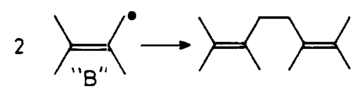
Table II. Compounds Isolated by Fractional Preparative GLC[a]

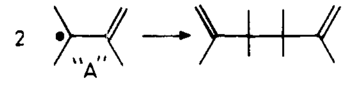
Sample[b]	Peak	Purity,[c] %	Major impurities[c]
A	4	73	1/2/3 (9%) 5/6/7 (17%)
B	6	46	4 (40%) 8/9 (14%)
C	8/9	49	4 (8%) 5/6/7 (42%)
D	14	83	11/12 (5%) 13 (4%) 15 (8%)
E	15	74	14 (13%) 16 (8%) 17 (5%)
F	17	95	

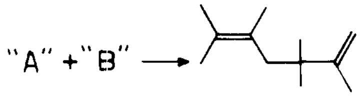
[a] Approximately 400 μL of each sample was obtained; for sample C, only 30 μL. [b] Other compounds were also isolated but at lower purity levels. [c] In each case, impurities correspond to major peaks of other samples.

at m/e 166, compound **16**, is probably a diolefinic compound.

Independent Synthesis of Some C_{12} Hydrocarbons. The independent synthesis of all the 21 C_{12} compounds should be extremely long and tedious. Moreover, some classical methods like Wurtz synthesis give mixtures of products, the problem being thereby only displaced. Nevertheless, preparation of some of the 21 C_{12} compounds may greatly help in determining the structure of the others. For this purpose we have submitted 2,3-dimethyl-2-butene to the action of DTBP and UV light. The combination of the A and B "forms" of the allylic A ↔ B radical gives three products, AA, AB, and BB.

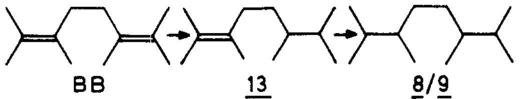

(B B) (12)


(A A) (13)


(A B) (14)

According to Cantrell,[21,22] essentially BB is formed, while Carless claims that BB and AB are obtained.[23] On packed columns (SE-30) only two peaks can indeed be seen. However, with an open tubular column of OV-1 at 110 °C, three products are detected[24] (Table III). They correspond to AB, AA, and BB, respectively, as evidenced by their ^1H NMR, ^{13}C NMR, and mass spectra.[25-27] It must be pointed out that chromatograms of the reaction of 2,3-DMB itself do not show important peaks corresponding to AA, AB, or BB.

The hydrogenation of BB leads to compound **13** and finally to a mixture of **8/9**. This confirms our assumption that peaks **8/9** correspond to the R_1R_1 dimers and allows also the identification of peak **13**.

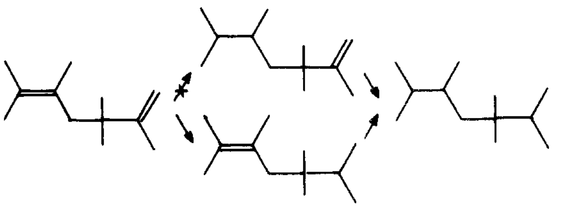

BB 13 8/9 (15)

The hydrogenation of AB leads to **14** and finally to **6**. Thus peak **6** corresponds to R_1R_3 and compound **17**, the third saturated dimer, must be R_3R_3. Two monoolefins are possible starting from AB. However, tetrasubstituted olefins are very difficult to hydrogenate compared to disubstituted olefins and no doubt is therefore possible concerning the exact nature of **14**.

Table III. Retention Times and GC Area Percentages for the C_{12} Hydrocarbons Obtained by the Action of DTBP on 2,3-Dimethyl-2-butene and 2,3-Dimethyl-1-butene

Peak	Retention times, min[a]	GC area percentages: 2,3-Dimethyl-2-butene	GC area percentages: 2,3-Dimethyl-1-butene
1	30.1		12.8
5	33.9		4.2
10′	38.5		0.7
12 + 12′	41.0[b]	34.0 + 14.0	26.1 + 10.7
12″	41.7		22.7
16	51.4[b]	52.0	22.8

[a] For the GC analysis conditions, see Experimental Section. [b] At 110 °C, compounds 12, 12′, and 16 elute at 24.7, 25.0, and 29.0 min, respectively.

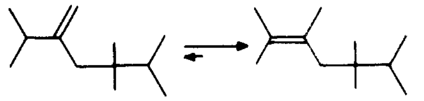

AB 14 6 (16)

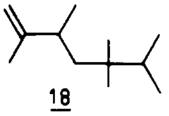
Hydrogenation of Reaction Mixtures. Hydrogenation of reaction mixtures obtained from the action of DTBP on 2,3-DMB itself confirms the preceding determinations and allows the identification of other peaks. Thus, the hydrogenation of a sample containing 68% **14** and 32% **15** gives a mixture containing 67% **6** and 33% **17**.

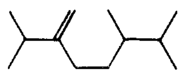
$$14 \rightarrow 6 \qquad (16')$$


15 17 (17)

With a mixture containing 57% **4**, 29% **6**, 6% **7** and 8% **8/9**, **4** is rapidly converted to **14** and then more slowly to **6**. The rapid reaction corresponds to an isomerization. Although the equilibrium is almost entirely displaced to the formation of **14**, the hydrogenation proceeds via the less substituted isomer **4** (and/or eventually its terminal isomer **18**). After complete hydrogenation, the mixture contains 84% **6** and 16% **8/9**. Therefore, compound **7** is a precursor of **8/9** and has most probably the structure CR_1.


4 14 (18)

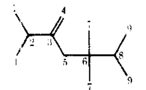
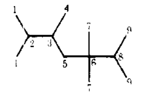
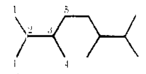
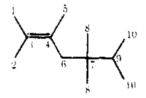
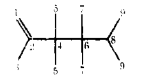

18


7

^{13}C NMR Spectroscopy. For alkanes, chemical shifts may be predicted from structural parameters. The Grant and Paul equation[28] extended by Carman, Tarpley, and Goldstein[29] does not give the 4°(4°), 3°(4°), 4°(3°), . . ., parameters required for highly branched dimers. The 4°(2°), 2°(4°), and 3°(3°) parameters are furthermore based on a single observation. We have used the relation proposed by Lindeman and Adams:[30]

$$\delta_C(k) = B_S + \sum_{M=2}^{4} D_M A_{SM} + \gamma_S N_{k3} + \Delta_S N_{k4} \qquad (19)$$

Table IV. Calculated and Experimental ^{13}C Chemical Shifts and Experimental ^{1}H Chemical Shifts for the C_{12} Hydrocarbons

			^{13}C NMR			^{1}H NMR
Registry no.	Hydrocarbon (solvent)	Carbon	Obsd shift (multiplicity)	Calcd shift	Δδ	Obsd shift (multiplicity)
62816-29-9	 **4** (CDCl$_3$ 50% v/v)	1	22.45 (q)	18.64–20.14	2.31	1.02 (d)
		2	34.86 (d)	32.53 ± ?		2.10 (m)
		3	154.49 (s)	154.20	0.29	
		4	109.66 (t)	109.51	0.15	4.68 (s); 4.89 (s)
		5	44.83 (t)	42.11	2.72	2.02 (s)
		6	36.52 (s)	34.85–36.35	0.17	
		7	24.31 (q)	23.79	0.52	0.82 (s)
		8	37.09 (d)	35.59	1.50	1.45 (m)
		9	17.68 (q)	16.15	1.53	0.86 (d)
52670-35-6	 **6** (CDCl$_3$ 95% v/v)	1	18.09 (q)	19.14	-1.05	*d*
			20.29 (q)		1.15	
		2	32.23 (d?)	32.53	-0.30	*d*
		3	34.33 (?)	34.99	-0.66	*d*
		4	17.87 (q)	17.13	0.74	*d*
		5	44.15 (t)	42.71	1.44	*d*
		6	35.72 (s)	35.35	0.37	
		7	24.33 (q)	24.29	0.04	0.83 (s)
		8	36.71 (?)	36.09	0.62	*d*
		9	17.67 (q)	16.15	1.52	*d*
62816-30-2 62816-31-3	 **8/9** (CDCl$_3$ 95% v/v)	1	18.09 (q)	19.14	-1.05	0.80 (d)
			20.29 (q)		1.15	
		2	32.23 (d?)	32.53	-0.30	1.45 (m)
		3	38.97 or	39.13	-0.16	1.45 (m)
			39.14 (d?)		0.01	
		4	15.51 (q)	16.15	-0.64	*d*
		5	32.02 (t?)	31.53	0.49	1.20 (m)
62816-32-4	 **14** (CDCl$_3$ 50% v/v)	1	*a* (q)	19.14 ± ?		1.65 (s)
		2	*a* (q)	19.14 ± ?		1.65 (s)
		3	126.48 (s)[b]	128.02	-1.54	
		4	126.96 (s)[b]	128.49	-1.53	
		5	*a* (q)	17.13 ± ?		1.65 (s)
		6	43.37 (t)	42.11	1.26	2.04 (s)
		7	38.20 (s)	34.85–36.35	1.85	
		8	24.72 (q)	23.79	0.93	0.81 (s)
		9	38.50 (d)	35.59	2.91	1.55 (m)
		10	17.79 (q)	16.15	1.64	0.88 (d)
62816-33-5	 **15** (CDCl$_3$ 75% v/v)	1	113.18 (t)	109.51	3.67	4.82 (s); 4.88 (s)
		2	152.82 (s)	154.20	1.38	
		3	23.93 (q?)	17.13 ± ?		1.83 (s)
		4	45.21 (s)	40.44 ± ?		
		5	25.39 (q)	17.81–19.31	6.08	1.08 (s)
		6	40.72 (s)	39.94–41.44	-0.72	
					0.78	
		7	21.39 (q)[c]	17.81	3.58	0.84 (s)
		8	31.65 (d)	31.45	0.20	?
		9	20.90 (q)[c]	17.68	3.22	0.86 (d)
52670-36-7	 **17** (CDCl$_3$ 55% v/v)	1	21.09 (q)	17.13	3.96	0.91 (d)
		2	32.42 (d)	31.95	0.47	1.98 (m)
		3	41.50 (s)	40.44	1.06	
		4	21.87 (q)	18.31	3.56	0.83 (s)

[a] Peaks are observed at 22.08, 21.70, and 20.91 ppm. The exact attribution to each olefinic methyl is difficult. By comparison with *cis*- and *trans*-2-butenes and with other cis and trans 2-alkenes, it seems reasonable to attribute these three signals to carbons 1, 5, and 2, respectively. [b] The attribution is not certain and may be inverted. However, calculations give a slightly higher shift value for carbon 4. [c] The attributions for carbons 7 and 9 are questionable. [d] Compounds **6** and **8/9** being a mixture, exact attributions are not straightforward. For compound **6** a doublet (6 hydrogens) is observed at 0.84 ppm.

This more elaborated relation is also based on a larger number of observations.

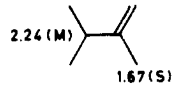
For olefinic carbons and for aliphatic carbons in unsaturated molecules, we have used the parameters and estimations proposed by Roberts.[31] Table IV compares calculated and observed shifts. The agreement is generally fairly good. It is, however, poorer for the most branched compounds **15** and **17**. This proves that the relation 19 does not yet take into account all the possible structures and that additional parameters should be necessary in order to improve the precision of the predictions, for example, replacement of γ by A_{SM}-type parameters, as already suggested by Lindeman and Adams.[30] It seems also that the rules defined by Roberts for olefins were obtained from a too limited set of molecules and may not apply with great accuracy to very branched compounds.

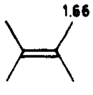
^{1}H NMR Spectroscopy. The proton chemical shifts of the C_{12} compounds are given in the last column of Table IV. The identification of compound **4** (fraction A) is confirmed by comparison with 2,3-dimethyl-1-butene and 2,2,3-trimethylbutane (**19**). Compound **6** (fraction B) does not reveal the

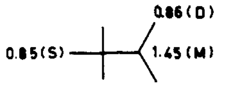
Table V. Physical Properties of Some C_{12} Hydrocarbons

Hydrocarbon	Bp, °C	d^{20}_4	n^{20}_D	IR ref	^{1}H NMR ref
R_1R_1 (**8**/**9**)	92 (20–22 mm)^{33}	0.7593^{a,33}	1.42527^{a,33}		*b*
AB (**12**)	183.0		1.4653	23	23, 27
BR_3 (**14**)	193^c		1.4365^c		*b*
BB (**16**)	81–82 (13 mm)^{35}	0.8081^{35}	1.4623^{35}	23	21, 23, 34
	87.5–88.5 (18 mm)^{33}	0.7971^{a,33}	1.45963^{a,33}		
	81–83 (14 mm)^{36}				
	202.7		1.4642		27
	38–40 (0.01 mm)^{22}				
	100 (30 mm)^{d,34}				
R_3R_3 (**17**)	208.5		1.4592		*b*

^{a} At 25 °C. ^{b} See Table IV. ^{c} Purity 83% (see Table II). ^{d} Crude dimer.







19

presence of olefinic protons (all signals below 2 ppm). No important differences (except for the olefinic protons) can be evidenced between the spectra of **4** and **6**. This confirms that they have the same carbon skeleton. Olefinic protons are also absent in compounds **8**/**9** (fraction C). Spectra of compounds **14** (fraction D) and **15** (fraction E) can be reconstructed from 2,2,3-trimethylbutane (**19**), 2,3-dimethyl-1-butene, and 2,3-dimethyl-2-butene. The spectrum of **17** (fraction F) must of course be the simplest one.

Physical Properties of the C_{12} Hydrocarbons. Of the 21 C_{12} hydrocarbons only one alkane, R_1R_1,[32,33] and two diolefins, AB[23] and BB,[21–23,33–36] have been mentioned in the literature. Table V collects the available information this work included. The values for R_3R_3 confirm the particular behavior of biquaternary compounds: they present much higher values for their refractive index and boiling point. The refractive index of most dodecanes lies in the range 1.4200–1.4300.[37] 2,4,4,5,5-Pentamethylheptane with two adjacent quaternary carbons has a value of 1.4402,[38] still significantly lower than that of R_3R_3 whose two vicinal quaternary carbons are flanked by tertiary ones! Quite branched dodecanes have generally boiling points below 200 °C. Once more, R_3R_3 is an interesting exception.

Probable Identification of the Other Peaks. It is probable that in the reaction medium much less 2,3-dimethyl-1-butene is formed than the corresponding 2-butene. Primary radicals R_1 show less tendency to disproportionate than tertiary ones and R_3 will probably give the more stable 2-butene. Therefore compounds containing the C and D radicals must be less abundant and their identification more difficult. The dehydrodimerization of 2,3-dimethyl-1-butene alone permits us, however, to make valuable suppositions concerning the nature of compounds not yet identified.

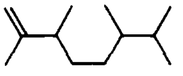
The action of peroxide and light on 2,3-dimethyl-1-butene leads in principle to the formation of ten diolefins from the A $\leftrightarrow$ B, C, and D radicals. In practice seven peaks are observed by capillary GLC (Table III). Four peaks (**1**, **5**, **10′**, and **12″**) are not formed with the 2-butene. They must therefore contain the C (or, less probably, the D) radical. The two major peaks (**1** and **12″**) must of course correspond to AC and BC. From chromatographic data (to be discussed in the next paragraph), AC corresponds to peak 1 and BC to peak 12″. Therefore, peak **5** should correspond to CC. Only compounds containing the less probable D radical (AD, BD, CD, and DD) have not yet been attributed. Peak **10′** is tentatively attributed to BD (rather than to AD because form B is more abundant than form A in the dehydro dimers). Compounds CD and DD must be negligible.

By adjusting the initial concentrations of 2,3-DMB and one of the 2,3-dimethylbutenes, one must favor the formation of monoolefinic C_{12} hydrocarbons. In fact, the reaction of 2,3-dimethyl-2-butene(1 part) and 2,3-DMB (4 parts) leads to the increased formation of the monoolefins BR_3 and AR_3 (peaks **14** and **15**). Under similar conditions we observed with 2,3-dimethyl-1-butene an increase of peaks 4 (CR_3), **14**, and **15**.

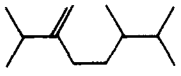
Except for peaks **2**, **3**, and **7**, all the peaks of Table I have been attributed. Since peaks **2** and **3** appear always in quite similar proportions, they may correspond to the threo and erythro isomers of DR_1. At 137 °C, the importance of these two peaks is enhanced (Table I). This should correspond to a larger proportion of attack on the primary sites with an increase of the reaction temperature.[39] Therefore, only peak **7** remains unattributed. It corresponds probably to CR_1 which has not yet been found.

Boiling Temperatures and Chromatographic Retention Times. Attributions made in the last paragraph are plausible suppositions concerning products which were not isolated from the reaction medium or synthesized by an independent reaction. These suppositions are also in agreement with chromatographic considerations.

The presence of a tetrasubstituted double bond increases the boiling temperature of a hydrocarbon while the introduction of a 1,1-disubstituted double bond decreases it (2,3-DMB, 58.0 °C; 2,3-dimethyl-2-butene, 73.2 °C; 2,3-dimethyl-1-butene, 55.7 °C). The influence of an unsaturation must be less in the C_{12} than in the C_6 compounds. Moreover, different 1,1-disubstituted olefins exist, for example, CR_1 and DR_1. With terminal olefins, the temperature lowering is larger. Although branching generally lowers boiling temperatures, an increase is, however, observed when two quaternary carbon atoms are vicinal. Alkanes, alkenes, and nonconjugated alkadienes, which are all of low polarity, elute on a nonpolar column like silicone OV-1, approximately according to their boiling temperature. From this point of view the observed retention time sequences 20 to 22 not only confirm the identifications made but are also in accordance with the attributions reported in the preceding paragraph.

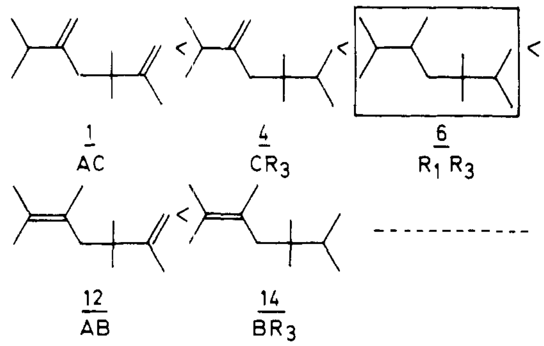


DR_1



CR_1

Of all the possible C_{12} compounds, two monoolefins and three diolefins do not appear on the chromatograms. Similar considerations lead us to suppose that AD should be eluted before peak **1**, DD approximately at the same time, and CD not far after it. DR_3 and AR_1 should be eluted between peaks



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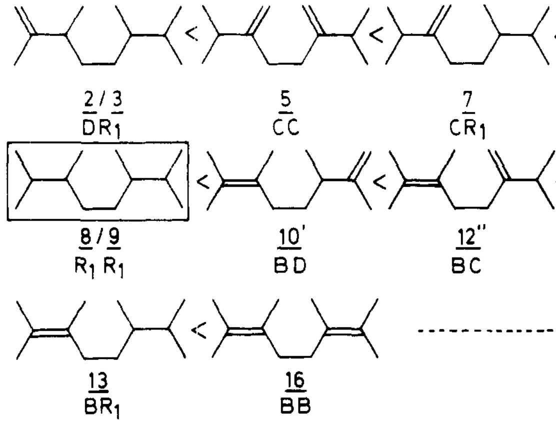

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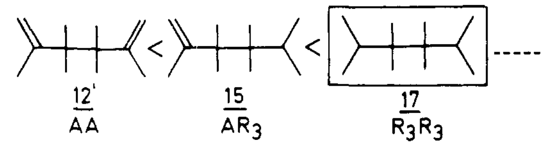

(22)

1 and 4.[39] Table VI summarizes the C_{12} hydrocarbons formed by combination of the different radicals.

Importance of the Various Radicals. It is not possible from these reactions to determine exactly the relative reactivities of the tertiary and primary hydrogen atoms in 2,3-DMB. In fact, the A ↔ B, C, and D radicals may arise from R_1 as well as from R_3. If they originate only from R_1, Table I leads to a relative reactivity of 8.4. In the other borderline case (all radicals originating from R_3 only) a value of 40.2 is determined. In the chlorination of 2,3-DMB by *tert*-butyl hypochlorite, the relative reactivity tertiary/primary is near 40.[40–42] This value is due to *tert*-butoxyl radicals and not to chlorine atoms which are more reactive.[43] This leads us to conclude that the A ↔ B, C, and D radicals are generated more by R_3 than by R_1. In other words, tertiary radicals show a greater tendency to disproportionate than primary ones do.[2]

With allyl radicals, two resonance structures exist. For 2,3-dimethyl-2-butene, we observe 34% AB, 14% AA, and 52% BB. Thus in the dehydro dimers the B structure is present to an extent of 69% and the A structure to an extent of 31%. These values do not necessarily represent exactly the importance of the A and B structures in the allyl radical itself because steric hindrance to dimerization is not impossible for A. Nevertheless, the predominance of B structures has already been mentioned for the chloroallyl radical **20**[44]

$$\underset{\mathbf{20B}}{\mathrm{ClCH{=}CHCH_2\cdot}} \leftrightarrow \underset{\mathbf{20A}}{\mathrm{Cl\dot{C}HCH{=}CH_2}}$$

and for the methoxypentenyl radical **21**.[45]

$$\underset{\mathbf{21B}}{\mathrm{CH_3OCH_2CH_2CH{=}CHCH_2\cdot}} \leftrightarrow \underset{\mathbf{21A}}{\mathrm{CH_3OCH_2CH_2\dot{C}HCH{=}CH_2}}$$

Table VI. C_{12} Hydrocarbons Formed by Combination of Indicated Radicals (Photochemical Reaction at 35 °C. Composition given in Percentage of GC Area. Peaks Numbers Are Given in Parentheses)

	R_3	R_1	C	B	A	D
D	*a*	2.3 (**2/3**)[a]		(**10'**)		
A	4.8 (**15**)	*a*	Tr (**1**)	Tr (**12**)	Tr (**12'**)	
B	12.5 (**14**)	0.4 (**13**)	Tr (**12''**)	Tr (**16**)		
C	32.8 (**4**)	2.0 (**7**)	1.8 (**5**)			
R_1	13.7 (**6**)	3.8 (**8/9**)				
R_3	25.9 (**17**)					

[a] See, however, note 39.

For 2,3-dimethyl-1-butene, two different allylic hydrogen atoms can be abstracted. Table III indicates that the extent of the different structures in the dehydro dimers is A, 30.3%; B, 47.7%; and C, 22.0%. Thus, for the A ↔ B resonating radical, *the importance of the two structures (38 and 62%) is close to* the results obtained with the 2-butene (31 and 69%). The primary allylic hydrogen atoms are only 1.2 less reactive than the tertiary ones. This may be explained by the high reactivity of allylic positions. Finally, radical D is almost absent at ordinary temperature but takes probably more importance in the thermal reaction.

In the γ-radiolysis of 2,3-DMB, the relative reactivities tertiary/primary are much lower: 0.7 and 10.0 for the two extreme cases (Table I). Although part of the products may be due to ionic reactions, the differences are large enough to conclude that the peroxide is much more selective than γ-radiations.

Registry No.—**19**, 464-06-2; BB, 18495-18-6; AA, 62816-34-6; AB, 53256-17-0; DTBP, 110-05-4; 2,3-DMB, 79-29-8; 2,3-dimethyl-2-butene, 563-79-1; 2,3-dimethyl-1-butene, 563-78-0.

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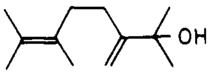
(25) During the preparative VPC, the two first peaks elute together but an important part of the second product disappears. This again is an indication of the AA structure, the most unstable of the three diolefins.

(26) On standing at room temperature for weeks in a closed Pyrex bottle, the diolefin BB gradually disappears although the liquid remains perfectly colorless. The capillary chromatograph reveals a new product eluting after *n*-dodecane. It is in fact the tertiary alcohol **22** as evidenced by ^{1}H NMR, ^{13}C NMR, IR, and mass spectrometry. Such a reaction is known to proceed rapidly in the presence of sensitizers like benzophenone.[46,47]



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(27) Spectroscopic data follow. Compound BB (neat): ^{1}H NMR 1.63 (s); 2.05 (s); ^{13}C NMR 20.58, 20.02, and 18.65 (q), 33.61 (t), 123.73 and 128.02 (s). Compound AB (neat but slightly contaminated by AA): ^{1}H NMR 1.05, 1.65, 1.78, and 2.19 (s), 4.78 (m); ^{13}C NMR 20.00, 20.80, 21.57, and 27.53 (q), 45.30 and 109.56 (t), 40.81, 126.45, 126.84, and 153.11 (s). Compound AA (diluted in AB): ^{1}H NMR 1.08 and 1.81 (s), 4.89 (br s); ^{13}C NMR 151.92 (s), 44.25 (s?), 114.10 (t?), 24.71 (q), 23.45 (q?).

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Kinetics of the Interaction of Nitrosobenzenes with Substituted Benzaldehyde Phenylhydrazones

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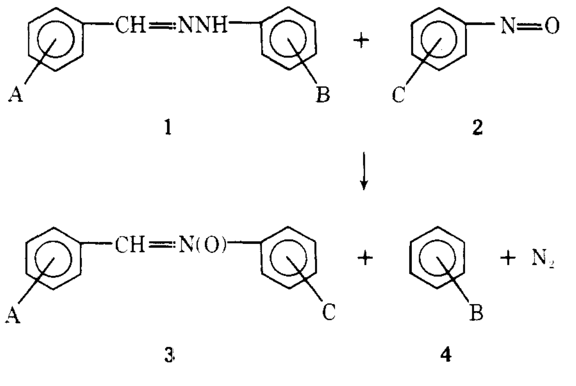
The reaction of benzaldehyde phenylhydrazone with nitrosobenzene follows second-order kinetics in either air or nitrogen at ambient temperature. Rates of reactions under nitrogen utilizing reactants substituted at meta and para positions of each of the three available aromatic rings have been correlated using the Hammett treatment. Reactions are facilitated by electron-donating substituents on benzaldehyde phenylhydrazones and by electron-withdrawing substituents on nitrosobenzenes. Oxygen exerts a more dramatic inhibition on reaction rates of substituted substrates than of parent compounds.

Benzaldehyde phenylhydrazone reacts with nitrosobenzene at ambient temperature to give nitrones, nitrogen, and benzene.[1] Phenylhydrazone derivatives of aromatic ketones and substituted benzaldehydes yield the corresponding nitrones, and product yields are sensitive to oxygen. The probable course of the reaction using reactants substituted at various aromatic rings may be summarized as shown in Scheme I.

Scheme I



Kinetics of this reaction have been studied to determine the order of the initial reaction of nitrosobenzenes with hydrazone substrates and to explore causes for oxygen sensitivity. The consequence of substitution (A, B, and C) at the aromatic rings has been investigated in order to elucidate the impact of electronic effects on the reaction.

Results and Discussion

General applicability of Scheme I is illustrated both by earlier synthetic work,[1] in which A- and B-ring substitution was investigated, and by formation of α-phenyl-N-m-chlorophenylnitrone (**3**, A = H, C = m-chloro) from reaction of m-chloronitrosobenzene with benzaldehyde phenylhydrazone (BPH). All three rings of reactants therefore could provide sites for substitution in this reaction system.

Initial kinetic investigations centered on the interaction of (unsubstituted) BPH with nitrosobenzene, and results indicated first-order rate dependency on both reactants. Plots of 1/(nitrosobenzene absorbance) vs. time for reactions in benzene, using equal initial concentrations of both reactants, were shown to be linear for at least three half-lives under *both* air and nitrogen atmospheres (average correlation coefficients of 0.9996 and 0.9995, respectively). It therefore was considered