REACTIVITY OF CYCLOALKENES IN THE RADICAL ADDITION REACTION WITH ETHYL CYANOACETATE*

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The effect of ring size on the reactivity of C_5 to C_{12} cycloalkenes in the copper(II) oxide catalysed and dibenzoyl peroxide initiated addition reaction with ethyl cyanoacetate was determined at 90°C using the method of competition reactions. *cis*-Cyclooctene exhibited the highest and cyclohexene as well as *cis*-cyclodecene the lowest reactivity. Relative reactivities of C_5, C_6 *cis*-C_7 and *cis*-C_8 cycloalkenes could be correlated with the Allinger's strain energies. In the copper(II) oxide catalysed reaction, the relative reactivities of cycloalkenes were surprisingly higher than in the dibenzoyl peroxide initiated reaction; this result is indicative of certain differences in the mechanisms of the initiation and propagation steps in both systems. The radical addition of ethyl cyanoacetate to cycloalkenes represent a novel and convenient route to alkyl α-cyanocycloalkaneacetates.

The effect of ring size on the reactivity of alicyclic compounds has been established in a great number of reactions[1-4]. A study of this effect in the free-radical chain reactions received considerably less attention[3]; structure-reactivity relationships have been reported for the thermal decomposition of azocycloalkanes and their derivatives[3,5-7], 1,1'-diphenyldicycloalkanes[8] and tert-butyl cycloalkaneperoxycarboxylates[9] and for the radical substitution reactions of cycloalkanes[10,11]. Unfortunately, the mechanisms of these reactions are not entirely unambiguous. To our knowledge, the dependence of reactivity of cycloalkenes on ring size in the radical addition reactions involving exclusively the carbon–carbon double bond has not so far been investigated systematically.

The purpose of this work has been to determine the effect of ring size of $C_5 - C_{12}$ cycloalkenes on rate of the radical addition reaction with ethyl cyanoacetate, either catalysed by copper(II) oxide or initiated by dibenzoyl peroxide. In addition, a comparison with some non-radical addition reactions was hoped to provide useful informations on the characteristics of this effect.

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EXPERIMENTAL

Chemicals. Ethyl cyanoacetate (Fluka AG., Buchs) was purified by rectification until chromatographically pure; b.p. 96°C/1·6 MPa, content of water 0·02% by mass. Cycloalkenes (Fluka AG.) were freed of peroxides by passage through a column of activated alumina and then redistilled (bulb to bulb) in an atmosphere of nitrogen. The purity of cyclopentene, cyclohexene and *cis*-cyclodecene was $>$99%, that of *cis*-cycloheptene and *cis*-cyclooctene $>$98%; according to the IR spectra[12] and ^{13}C-NMR spectra, cyclododecene contained 30–35% of the *cis* and 65–70% of the *trans* isomer and less than 1% of impurities. Dibenzoyl peroxide (Lachema, Brno) and di-tert-butyl peroxide (Koch-Light, Ltd, Colnbrook) were used as obtained. The preparation of copper(II) oxide by oxidation of copper powder in a stream of oxygen was described in a previous paper[13].

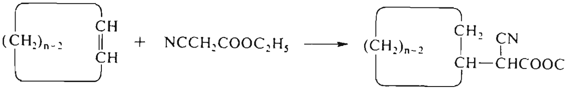
Ethyl esters of α-cyanocycloalkaneacetic acids. Authentic samples of esters were prepared according to the following general procedure: A mixture of cycloalkene and di-tert-butyl peroxide was gradually added during 1–2·5 h to ethyl cyanoacetate (molar ratio of cycloalkene to peroxide and ester = 1 : 0·2 : 10) placed in a 50 ml glass vessel equipped with a thermometer and reflux condenser; the mixture was magnetically stirred in an atmosphere of nitrogen at 145°C. After an additional heating for 1 h, when the cycloalkene conversion attained 90–98%, the reaction mixture was cooled to room temperature and transferred into a Hickman flask. The unreacted ethyl cyanoacetate and cycloalkene as well as a small amount of methylcycloalkane, which resulted from the interaction of cycloalkene with the product of peroxide fragmentation, were distilled off to afford a yellow oily residue. Distillation of the residue *in vacuo* gave in all cases the analytically pure 1 : 1 adduct and a small amount of undistillable telomers. Ethyl α-cyanocyclopentaneacetate (yield of pure product 62%), b.p. 92°C/120 Pa (ref.[14] b.p. 137 to 138°C/2·53 kPa; purity 95%). For $C_{10}H_{15}NO_2$(181·2) calculated: 66·27% C, 8·37% H; found: 66·22% C, 8·33% H. Ethyl α-cyanocyclohexaneacetate (yield 51%), b.p. 99–100°C/93 Pa (ref.[15] b.p. 112–113°C/240 Pa). For $C_{11}H_{17}NO_2$ (195·3) calculated: 67·66% C, 8·78% H; found: 67·62% C, 8·73% H. Ethyl α-cyanocycloheptaneacetate (yield 53%), b.p. 118°C/173 Pa (ref.[16] b.p. 134–139°C/400 Pa). For $C_{12}H_{19}NO_2$ (209·3) calculated: 68·86% C, 9·15% H; found: 68·81% C, 9·10% H. Ethyl α-cyanocyclooctaneacetate (yield 41%), b.p. 125–126°C/107 Pa (ref.[17] b.p. 144–146°C/400 Pa). For $C_{13}H_{21}NO_2$ (223·3) calculated: 69·92% C, 9·48% H; found: 69·93% C, 9·36% H. Ethyl α-cyanocyclodecaneacetate, a new compound (yield 40%), b.p. 150°C : : 133 Pa. For $C_{15}H_{25}NO_2$ (251·4) calculated: 71·67% C, 10·03% H; found: 71·82% C, 10·00% H. Ethyl α-cyanocyclododecaneacetate, a new compound (yield 27%), b.p. 161°C/107 Pa. For $C_{17}H_{29}NO_2$ (279·4) calculated: 73·07% C, 10·46% H; found: 73·04% C, 10·35% H. All the α-cyano esters thus prepared showed identical IR spectra (neat, max.): ($C{=}O$) (s) 1745 ± 5, ($C{\equiv}N$) (w) 2255 ± 5 cm^{-1} (ref.[15] gives for ethyl α-cyanocyclohexaneacetate: ($C{=}O$) 1745, ($C{\equiv}N$) 2250 cm^{-1}). ^1H-NMR spectra (in $CDCl_3$ in relation to TMS) of all α-cyano esters exhibited peaks corresponding, in addition to those of the ring methylene groups, to the characteristic fragment $—CH(CN)COOCH_2CH_3$: δ (p.p.m): 4·2 ($\underline{CH}_2CH_3$, q, $J = 7$ Hz); 1·3 ($CH_2\underline{CH}_3$, t, $J = 7$ Hz); 3·4 (CHCN, d, $J = 6$ Hz) (ref.[15] gives for ethyl α-cyanocyclohexaneacetate: δ (p.p.m): 4·23 ($\underline{CH}_2CH_3$), 1·32 ($CH_2\underline{CH}_3$), 3·36 (CHCN)).

Competition reactions. cis-Cyclooctene, a cycloalkene, ethyl cyanoacetate and copper(II) oxide or silver(I) oxide or dibenzoyl peroxide were mixed in a molar ratio of 1 : 1 : 100 : 0·2 and the mixture was vibrationally stirred and heated under nitrogen in a sealed glass ampoule (10 ml) at 90°C. The addition reaction was stopped in the initial stage, *i.e.* at 5 to 25% conversions of cycloalkenes, and the composition of the resulting reaction mixture was determined by gas–liquid chromatography. As shown by analysis, the corresponding 1 : 1 adducts, *i.e.* the ethyl esters of α-cyanocycloalkaneacetic acids, were the only volatile products of the competitive addition reactions performed in the presence of metal oxides. The competition reactions were repeated at least three times, always with different conversions of cycloalkenes. The resulting relative reactivities were expressed by the k_8/k_n and k_n/k_6 ratios. The course of the heterogeneous competition reactions catalysed by copper(II) oxide (*vide supra*) was checked in one case by conducting the reaction in a homogeneous system: Ethyl cyanoacetate and copper(II) oxide present in a molar ratio of 100 : 0·2 were heated with magnetical stirring in an atmosphere of nitrogen at 80°C for 2 h. The mixture was cooled to room temperature, the undissolved copper(II) oxide was filtered off under nitrogen and an equimolar mixture (1 : 1) of *cis*-cyclooctene and cyclohexene was added at once under nitrogen to the filtrate containing Cu in a concentration of 1·4 . 10^{-3}M. The resulting mixture was then allowed to react at 90°C according to the above procedure. The relative reactivity expressed by the k_8/k_6 ratio corresponded to 4·75/1·00.

Analytical methods. The conversions of cycloalkenes, purity of cycloalkenes and products of the addition reactions as well as the molar ratios of ethyl α-cyanocyclooctaneacetate to ethyl α-cyanocycloalkaneacetate in reaction mixtures resulting from the competition experiments were determined by gas chromatographic analysis on a Chrom 41 instrument (Laboratory Instruments, Prague) equipped with a flame-ionization detector and a stainless-steel column (1·2 m × 3 mm) packed with 3% Silicone OV 17 on Gas-Chrom Q (80 – 100 mesh). The molar ratios of 1 : 1 adducts in the reaction mixture were calculated from the chromatographic data by correcting the ratios of the peak heights according to the calibration curves; the chromatograph was calibrated before each series of analytical measurements. The IR spectra of liquid films of α-cyano esters were recorded on a double-beam Zeiss (Jena), Model UR 20, spectrophotometer. The ^{1}H-NMR spectra of α-cyano esters and ^{13}C-NMR spectra of *cis*- and *trans*-cyclododecene were measured in $CDCl_3$ solutions with TMS as the internal standard using a Varian XL-200 spectrometer.

RESULTS AND DISCUSSION

The radical additions of ethyl cyanoacetate across the unsaturated linkage of alkenes catalysed by copper(II) oxide have been found to proceed with high selectivity[18,19]. As is evidenced in this work, the same holds also for an alicyclic carbon–carbon double bond and its interaction with ethyl cyanoacetate under the above conditions is therefore a model system suitable for determining the relative reactivities of cycloalkenes in a radical addition reaction. At the same time, this reaction represents a novel and convenient route to the corresponding alkyl α-cyanocycloalkaneacetates *I* ($n = 5-12$) (Eq. (*A*)).



(A)

I

Copper(II) oxide used as the catalyst reacts with ethyl cyanoacetate to form a soluble copper complex which is the active species of the catalyst participating in the initiation, possibly propagation step[13]. For the sake of comparison, dibenzoyl peroxide was chosen as a typical peroxidic initiating agent. The relative reactivities of C_5 to C_{12} cycloalkenes were determined in a series of competition experiments by the method of the initial reaction rates[20]. The relative rate constants for the addition reactions of *cis*-cyclooctene–cycloalkene pairs expressed by the k_8/k_n ratios are given in Table I. The dependence of the relative reactivities on ring size, with cyclohexene chosen as the reference cycloalkene, is illustrated in Fig. 1. As is seen from Fig. 1, in the copper(II) oxide catalysed as well as dibenzoyl peroxide initiated reaction *cis*-cyclooctene exhibits the highest and cyclohexene or *cis*-cyclodecene the lowest reactivity. Nevertheless, the differences in the relative reactivities of cycloalkenes are small and vary within one order of magnitude (Table I). However, the dependences presented in Fig. 1 also show that, surprisingly, the relative reactivities of cycloalkenes in reactions catalysed by copper(II) oxide are on the average 1·3 times as high as those observed in the dibenzoyl peroxide initiated reaction. This difference was found to be not caused by the heterogeneous nature of the catalyst. An identical reactivity of *cis*-cyclooctene relative to cyclohexene was observed in a homogeneous addition reaction which was catalysed by a soluble copper complex formed by interaction of copper(II) oxide with ethyl cyanoacetate (see Experimental).

There is no doubt that the addition reaction (Eq. (*A*)) catalysed by copper(II) oxide or copper complex[13] as well as that initiated by dibenzoyl peroxide follows a radical mechanism. This is witnessed also by an excellent linear log-log correlation between the relative rate constants $(k_n/k_6)_{CuO}$ and $(k_n/k_6)_{DBP}$ (correlation coefficient $r = 0{\cdot}9945$) demonstrated in Fig. 2.

TABLE I

Ratio of Rate Constants k_8/k_n for the Copper(II) Oxide Catalysed and Dibenzoyl Peroxide (DBP) Initiated Addition of Ethyl Cyanoacetate to *cis*-Cycloalkenes (*cis*-C_n)

cis-C_n	k_8/k_n	
	CuO	DBP
C_5	1·29 ± 0·04	1·08 ± 0·04
C_6	4·80 ± 0·08	3·10 ± 0·12
C_7	1·59 ± 0·07	1·44 ± 0·03
C_8[a]	1·00	1·00
C_{10}	4·30 ± 0·06	2·80 ± 0·07
C_{12}[b]	2·05 ± 0·06	1·55 ± 0·04

[a] The reference compound; [b] the hydrocarbon was a mixture of 30–35% *cis* and 65–70% *trans* isomer.

At first glance, there appears to be difficult to find an unambiguous explanation for the dependence of cycloalkene reactivities on the kind of the initiating agent (Figs 1 and 2). However, one cannot entirely rule out that the presence of a metal ion evokes some qualitative differences in the mechanism of the initiation and propagation steps. Aimed at elucidating this point we performed several competition experiments in which pairs of *cis*-cyclooctene–cyclohexene and *cis*-cyclooctene–*cis* + *trans*-cyclododecene were allowed to react with ethyl cyanoacetate under otherwise identical conditions, but in the presence of the less active silver(I) oxide as the initiator. We were able to prove that the relative reactivities of cycloalkenes differed only slightly from those found in a reaction catalysed by copper(II) oxide and corresponded to the following rate constant ratios: $k_8/k_6 = 4{\cdot}2$; $k_8/k_{12} = 1{\cdot}9$. Therefore, it appears that the cycloalkene reactivity may be affected by coordination or by another kind of interaction, not excluding a reaction which proceeds in the coordination sphere of a metal complex. Examples of such a reaction can be seen in the radical additions of tetrachloromethane to cyclohexene[21] and *cis*-cyclooctene[22]

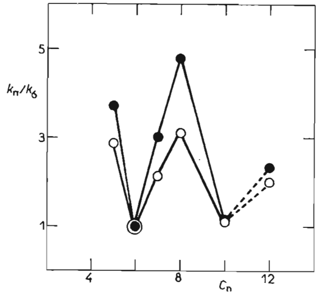


FIG. 1

Dependence of Reactivity of *cis*-Cycloalkenes on Ring Size (C_n) in the Copper(II) Oxide Catalysed (●) and Dibenzoyl Peroxide Initiated (○) Competitive Addition Reactions with Ethyl Cyanoacetate and Cyclohexene as Reference Compound

Cyclododecene was a mixture of 30 to 35% *cis* and 65—70% *trans* isomer.

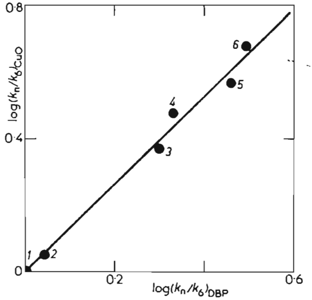


FIG. 2

Log-Log Correlation of Relative Reactivities of Cyclohexene (*1*), *cis*-Cyclodecene (*2*), *cis* + *trans*-Cyclododecene (*3*), *cis*-Cycloheptene (*4*), Cyclopentene (*5*) and *cis*-Cyclooctene (*6*) in the Copper(II) Oxide Catalysed [$\log(k_n/k_6)_{CuO}$] and Dibenzoyl Peroxide (DBP) Initiated [$\log(k_n/k_6)_{DBP}$] Addition Reaction with Ethyl Cyanoacetate catalysed by $RuCl_2[P(C_6H_5)_3]_3$. The coordination assumed above is also in harmony with the trend of the equilibrium constants reported for the formation of silver nitrate–cycloalkene complexes[23] (Table II); this trend is identical with that of the relative reactivites found for the reaction investigatied in this work (Eq.(*A*)). Another and presumably even stronger support for the involvement of coordination of a metal

TABLE II

Ratios of Rate Constants k_n/k_6 for Various Types of Reactions of Alicyclic Compounds

Reactions	k_n/k_6						
	C_5	C_6	C_7	C_8	C_{10}	C_{12}	Ref.
cis-Cycloalkenes							
Addition of ethyl cyanoacetate: catal. by CuO	3·72	1·0	3·02	4·80	1·12	2·34[a]	—[b]
init. by DBP	2·87	1·0	2·15	3·10	1·11	2·00[a]	—[b]
Ozonolysis	4·3	1·0	2·6	6·2	0·76	0·61	25
Diimide reduction	15·5	1·0	12·1	17·0	0·85	0·64	26
Addition of diethylaluminium hydride	8·7	1·0	16·2	20·0	0·75	—	27
Addition of hexachlorocyclopentadiene	22·5	1·0	30·0	75·0	0·9	—	28
Addition of disiamylborane[c]	108·0	1·0	554·0	2 046·0	—	—	29
Formation of complexes with silver nitrate[d]	2·0	1·0	3·5	4·0	—	—	23
Formation of Cu(I) complexes[e]	5·89	1·0	8·51	23·44	—	—	24
Cycloalkanes and their derivatives							
Oxidation of cycloalkanes by oxygen[f]	2·5	1·0	—	15·0	15·0	6·2	39
Oxidation of cycloalkanes by chromium(VI) oxide	2·0	1·0	6·6	21·4	41·6	3·9	40
Oxidation of cycloalkanols by lead tetraacetate:							
to ketones	1·4	1·0	1·8	5·1	7·4	6·0	41
to ethers	—	1·0	18·7	45·0	34·3	10·6	41
Thermal decomposition of azo-bis(cycloalcanecarbonitriles)	11·5	1·0	194·0	1 325·0	292·0	—	5
Thermal decomposition of tert-butylcycloalkaneperoxycarboxylates	0·5	1·0	2·3	4·3	3·3	1·9	9
Solvolysis of 1-chloro-1-methylcycloalkanes	124·0	1·0	108·0	286·0	17·7	—	42
Acetolysis of cycloalkyl *p*-toluenesulphonates	14·0	1·0	25·3	191·0	380·0	3·25	43

[a] Cyclododecene was a mixture of 30—35% *cis* and 65—70% *trans* isomer; [b] this work; [c] calculated from the data taken from ref.[26]; [d] ratio of the equilibrium constants taken from ref.[23]; [e] ratio of the stability constants $K_{Cu(I)}$ taken from ref.[24]; [f] data read from Fig. 1*a* in ref.[39].

ion comes from the fairly good linear log-log correlation ($r = 0{\cdot}9528$) of the stability constants $K_{Cu(I)}$ for the formation of copper(I)–cycloalkene complexes[24] (Table II) with our relative reactivities $(k_n/k_6)_{CuO}$. On the other hand, such a coordination must be absent in the presence of an organic peroxide used as the initiator. For this reason, we believe that the differences between the values of $(k_8/k_n)_{CuO}$ and $(k_8/k_n)_{DBP}$ are due presumably to coordination of the metal ion with the carbon–carbon double bond of cycloalkenes.

As there are no data in the literature which would concern the effect of ring size on the reactivity of cycloalkenes in the radical addition reactions involving exclusively the alicyclic carbon–carbon double bond, we compared our results with the relative reactivities of cycloalkenes in nonradical reactions, *i.e.* in the ozonolysis[25], diimide reduction[26], addition reactions of diethylaluminium hydride[27], hexachlorocyclopentadiene[28] and disiamylborane[29] as well as in the formation of complexes with silver nitrate[23] and of Cu(I) complexes[24] (Table II). The data in Table II reveal that *cis*-cyclooctene exhibits always the highest and cyclohexene, sometimes also

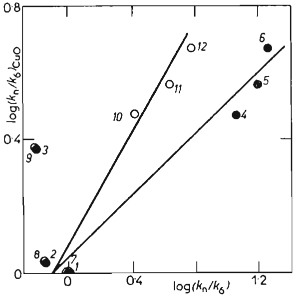


FIG. 3

Log-Log Correlation between the Relative Reactivities of Cyclohexene (*1*, *7*), *cis*-Cyclodecene (*2*, *8*), *cis* + *trans*-Cyclododecene (*3*, *9*), *cis*-Cycloheptene (*4*, *10*), Cyclopentene (*5*, *11*) and *cis*-Cyclooctene (*6*, *12*) in the Copper(II) Oxide Catalysed Addition Reaction with Ethyl Cyanoacetate [log $(k_n/k_6)_{CuO}$] and the Relative Reactivities [log (k_n/k_6)] in the Ozonolysis (○) and Diimide Reduction (●)

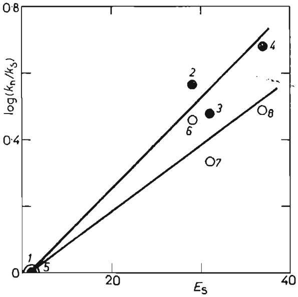


FIG. 4

Semi-Logarithmic Dependence of Relative Reactivities [log (k_n/k_6)] of Cyclohexene (*1*, *5*), Cyclopentene (*2*, *6*), *cis*-Cycloheptene (*3*, *7*) and *cis*-Cyclooctene (*4*, *8*) in the Copper(II) Oxide Catalysed (●) or Dibenzoyl Peroxide Initiated (○) Addition Reactions with Ethyl Cyanoacetate upon Allinger's Strain Energies E_S (kJ mol^{-1})

cis-cyclodecene, the lowest reactivity regardless of the reaction type. An analogous trend of reactivities (*cis*-C_8 > C_6) was found also for the epoxidation[30], acetoxylation[31] and homogeneous catalytic hydrogenation of cycloalkenes[32].

Relatively good correlations* are observed between log $(k_n/k_6)_{CuO}$ for the copper(II) oxide catalysed addition reaction of ethyl cyanoacetate and log (k_n/k_6) reaction of ethyl cyanoacetate and log (k_n/k_6) reported for the ozonolysis[25] and diimide reduction of cycloalkenes[26] (Fig. 3).

As Fig 4 shows, there exists also an acceptable linear correlation of log $(k_n/k_6)_{CuO}$ ($r = 0{\cdot}9812$) or log $(k_n/k_6)_{DBP}$ ($r = 0{\cdot}9501$) with the strain energies E_S in C_5, C_6, *cis*-C_7 and *cis*-C_8 cycloalkenes calculated recently by Allinger and Sprague[34] using the force-field method. This indicates that a common factor, such as the strain energy, determining the reactivity of cycloalkenes may be operative in these reactions. At this point it is to be noted that a reversed order of reactivities (C_6 > C_8) was reported to occur, for instance, in the heterogeneous catalytic hydrogenation[35,36], oxidation[37] and bromination of cycloalkenes[38].

From the data summarized in Table II it is further clear that in radical and ionic reactions cycloalkanes and their derivatives exhibit a reactivity – ring size dependence which is closely similar to that observed in some reactions of cycloalkenes; high reactivity is typical again for C_8 and sometimes C_{10} rings contrasting with the low reactivity of cyclohexane and its derivatives[5,9,39–43]. This trend of reactivity of cycloalkanes has been explained in accordance to the I-strain hypothesis involving $sp^3 \rightarrow sp^2$ changes at the reaction center in the transition state, which lead to a change in the ring strain. A reversed dependence of the reactivity on ring size is then exhibited by reactions of the $sp^2 \rightarrow sp^3$ type (ref.[1]).

In summary, the results show that the ring size – reactivity relationship found by us in the radical addition of ethyl cyanoacetate to cycloalkenes has analogies in some nonradical cycloalkene reactions as well as in radical and non-radical reactions of cycloalkanes. However, further experimental material is needed to account for the limited validity of these analogies and to support our explanation for the dependence of the cycloalkene reactivities on the kind of the initiating agent in the radical addition reactions with ethyl cyanoacetate. Research centered at these points is now in progress in our laboratory.

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* The relative reactivity of *cis* + *trans*-cyclododecene is an exception due presumably to the presence of the *trans* isomer (65–70%) which is known to exhibit greater reactivity[33]. The relative reactivities for *cis* + *trans*-cyclododecene given in this work are therefore clearly shifted to values which are larger than those which would pertain to pure *cis*-cyclododecene.

REFERENCES

1. Sicher J.: *Progress in Stereochemistry*, Vol. 3, p. 202. Butterworths, London 1962.
2. Goldfarb Y. L., Belenkii L. I.: Usp. Khim. *29*, 470 (1960).
3. Rüchardt C.: Usp. Khim. *47*, 2014 (1978).
4. Casanova J., Waegell B.: Bull. Soc. Chim. Fr. *1975*, 911.
5. Overberger C. G., Biletch H., Finestone A. B., Lilker J., Herbert J.: J. Amer. Chem. Soc. *75*, 2078 (1953).
6. Bonnekessel J., Rüchardt C.: Chem. Ber. *106*, 2890 (1973).
7. Hinz J., Rüchardt C.: Justus Liebigs Ann. Chem. *765*, 94 (1972).
8. Beckhaus H. D.: *Thesis.* Freiburg University, Freiburg 1974.
9. Lorenz P., Rüchardt C., Schacht E.: Chem. Ber. *104*, 3429 (1971).
10. Russel G. A.: J. Amer. Chem. Soc. *80*, 4997 (1958).
11. Rüchardt C.: Forschungsber. Landes Nord-Rhein-Westfalen, 1975, No 2471. Westdeutscher Verlag, Opladen 1975; Chem. Abstr. *87*, 84401 (1977).
12. Prelog V., Speck M.: Helv. Chim. Acta *38*, 1786 (1955).
13. Hájek M., Málek J.: This Journal *44*, 3695 (1979).
14. Albarella J. P.: J. Org. Chem. *42*, 2009 (1977).
15. Marshall J. A., Carroll R. D.: J. Org. Chem. *30*, 2748 (1965).
16. Royals E. E., Neal A. N.: J. Org. Chem. *21*, 1448 (1956).
17. Saharia G. S., Tyagi M. P.: J. Indian Chem. Soc. *44*, 601 (1967).
18. Hájek M., Málek J.: Synthesis *1977*, 454.
19. Hájek M., Málek J.: React. Kinet. Catal. Lett. *10*, 77 (1979).
20. Huyser E. S.: *Free-Radical Chain Reactions*, p. 59. Wiley-Interscience, New York 1970.
21. Matsumoto H., Nikaido T., Nagai Y.: Tetrahedron Lett. *1975*, 899.
22. Matsumoto H., Nakano T., Takasu K., Nagai Y.: J. Org. Chem. *43*, 1734 (1978).
23. Muhs M. A., Weiss F. T.: J. Amer. Chem. Soc. *84*, 4697 (1962).
24. Harvilchuck J. M., Aikens D. A., Murray R. C., jr: Inorg. Chem. *8*, 539 (1969).
25. Popov A. A., Razumovskii S. D., Parfenov V. M., Zaikov G. E.: Izv. Akad. Nauk SSSR, Ser. Khim. *1975*, 282.
26. Garbisch E. K., Schildcrout S. M., Patterson D. B., Sprecher C. M.: J. Amer. Chem. Soc. *87*, 2932 (1965).
27. Ziegler K., Gellert H. G., Martin H., Nagel K., Schneider J.: Justus Liebigs Ann. Chem. *589*, 91 (1954).
28. Ziegler K., Froitzheim-Kühlhorn H.: Justus Liebigs Ann. Chem. *589*, 157 (1954).
29. Brown H. C., Moerikofer A. W.: J. Amer. Chem. Soc. *85*, 2063 (1963).
30. Su Ch.-Ch., Reed J. W., Gould E. S.: Inorg. Chem. *12*, 337 (1973).
31. Guenzet J., Camps M.: Bull. Soc. Chim. Fr. *1973*, 3167.
32. Jardine I., McQuillin F. J.: Tetrahedron Lett. *1968*, 5189.
33. Balenkova E. S., Kochnova G. P., Karomov S. I.: Neftekhimiya *9*, 29 (1969).
34. Allinger N. L., Sprague J. T.: J. Amer. Chem. Soc. *94*, 5734 (1972).
35. Hussey A. S., Baker R., Keulks G. W.: J. Catal. *10*, 258 (1968).
36. Kajitani M., Sasaki Y., Okada J., Ohmura K., Sugimori A., Urushibara Y.: Bull. Chem. Soc. Jap. *47*, 1203 (1974).
37. Verstraelen L., Lalmand M., Hubert A. J., Teyssie P.: J. Chem. Soc., Perkin Trans. 2, *1976*, 1285.
38. Dubois J. E., Fresnet P.: Tetrahedron Lett. *1974*, 2195.
39. Koshel G. N., Faberov M. I., Jablonskii O. P.: Dokl. Akad. Nauk SSSR *222*, 360 (1975).
40. Mareš F., Roček J., Sicher J.: This Journal *26*, 2355 (1961).

41. Mihailovic M. L., Cekovic Z., Andrejevic V., Matic R., Jeremic D.: Tetrahedron *24*, 4947 (1968).
42. Brown H. C., Borkowski M.: J. Amer. Chem. Soc. *74*, 1894 (1952).
43. Heck R., Prelog V.: Helv. Chim. Acta *38*, 1541 (1955).

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