

DIPOLE MOMENTS OF SOME QUINONE METHIDES IN THE GROUND AND FIRST EXCITED STATES*

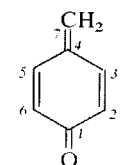
B.KOUTEK, M.PřISOVÁ, M.SOUČEK and O.EXNER

*Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, 166 10 Prague 6*

Received November 25th, 1975

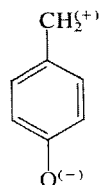
Dipole moments of ten quinone methides *I–III* were determined in the ground state from dielectric measurement in benzene solution, and in the first excited state from the solvent spectral shifts; the latter procedure has been improved as to the statistical treatment. The ground state moments of anthrone derivatives *III* are normal and correspond to an aromatic ketone. The values for the derivatives of fuchsone (*I*) and of 4-isopropylidene-2,5-cyclohexadienone (*II*) are higher but differ significantly from each other, suggesting a contribution of 9–18% of the dipolar mesomeric structure *B*. This amount is dependent on the steric effect of substituents in 2,6-positions. The excited state moments correspond to an enhanced contribution of the structure *B*, up to 40%, and are less dependent on structure. All the available data, including the carbonyl frequency and electronic spectra, suggest a strong conjugation within the quinone methide system whose intensity is, however, rather different in individual compounds and according to individual criteria.

In the course of our investigations on quinone methides^{1,2} we have encountered several times the problem of conjugation in this particular system which may be expressed by the mesomeric formulae $A \leftrightarrow B$. The conjugation may be formally classified as crossed but the weight of the dipolar formula *B* is enhanced by the presence of an aromatic system. A recent review³ reveals that very few physical measurements^{4,5} on the quinone methide system are available; simple HMO calculations³ then indicate a great importance of formula *B* corresponding to a π -electron charge of +0.39 on the carbon atom $C_{(7)}$.



$$\mu_{\text{calc}} \approx 2.5 \text{ D}$$

A

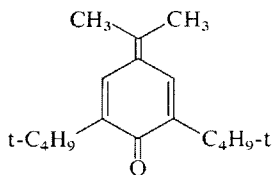
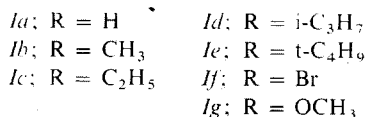
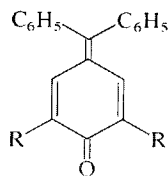


$$\mu_{\text{calc}} \approx 25.5 \text{ D}$$

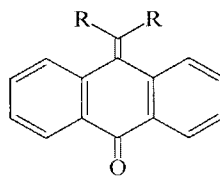
B

* Part VI in the series Quinone Methides and Fuchsones; Part V: see ref.².

In this paper we attempt to estimate the gross electron distribution of selected quinone methides *I–III* from their experimental dipole moments. The choice of compounds was dictated mainly by the instability of the simplest derivatives; in addition we wanted to follow the steric effects on conjugation in the molecules of *Ib–Ie* and the effect of annelation in *IIIa,b*. The ground state dipole moments (μ_g) were determined by solution measurement using the conventional technique. To estimate the dipole moments in the first electronically excited state (μ_e) we applied the method of solvent shifts in absorption spectra⁶ since the fluorescence spectra were not usable and in addition the approach based on them has some drawbacks⁶.



II



IIIa: R = H
IIIb: R = C₆H₅

The method⁶ of absorption-maximum shifts is based on the equation

$$\frac{\tilde{\nu}_j - \tilde{\nu}_i}{f(n_i^2) - f(n_j^2)} = A + \frac{2\mu_g \Delta\mu}{hca_0^3} \frac{f(\epsilon_i) - f(\epsilon_j)}{f(n_i^2) - f(n_j^2)}, \quad (1)$$

which relates the wavenumbers $\tilde{\nu}_i$ and $\tilde{\nu}_j$ in the *i*-th and *j*-th solvent, respectively, to the properties of these solvents expressed by the function *f* of their dielectric constant ϵ and their refractive index *n*. The function *f* has the usual form:

$$f(x) = (x - 1)/(2x + 1).$$

Assuming that the radius of the spherical cavity a_0 can be estimated, one can calculate the scalar product of the vectors μ_g and $\Delta\mu$, from experimental quantities; $\Delta\mu$ denotes the vector difference of the excited and ground state moments

$$\Delta\mu = \mu_e - \mu_g.$$

Since the molecules under study have approximately the C_{2v} symmetry (disregarding alkyl groups, not contributing significantly to the dipole moment), the vectors μ_g and μ_e are collinear and μ_e can be simply evaluated. There is, however, a defect of statistical nature in the original treatment⁶ since Eq. (1) was applied to all pos-

sible pairs of solvents, unless the difference $\tilde{\nu}_j - \tilde{\nu}_i$ was too small. Hence a plot was produced with much more points than are independent measurements. In addition to the incorrect number of degrees of freedom, there is another shortcoming in Eq. (1) that one independent variable (n) appears on both sides; both these defects simulate a better fit than it is in reality.

A statistically correct procedure involves multiplying Eq. (1) by $[f(n_i^2) - f(n_j^2)]$ to give

$$\tilde{\nu}_j - \tilde{\nu}_i = A[f(n_i^2) - f(n_j^2)] + B[f(\epsilon_i) - f(\epsilon_j)] + C. \quad (2)$$

One solvent (j) is then kept constant and the coefficient $B = 2\mu_g \Delta\mu/(hca_0^3)$ is obtained by multiple regression with the left-hand side of Eq. (2) as the dependent variable and the two bracketed terms as independent variables. There are as many points in the regression as the number of measurements, *i.e.* solvents. The intercept C should equal zero within the limits of its error; this may serve as an additional test of the theory.

The reliability of the whole calculation depends still on the estimation of a_0 . The common procedure⁷ is based on the additivity of the molar volume and assumes the spherical shape of the molecule. Hence it may be relied upon in the extent that comparable results may be obtained only for sterically similar molecules. This condition is approximately satisfied in the case of the compounds *I–III*.

EXPERIMENTAL AND RESULTS

Materials: The quinone methides *I–III* were prepared by known methods^{8–15}. Their melting points were determined on the Kofler block and are not corrected. The samples for analysis and physical measurements were dried 8 hours at 0.1 Torr at 20°C.

4-Benzhydrylidene-2,5-cyclohexadien-1-one (*Ia*), m.p. 166–168°C (literature⁸ 167–169°C) and 2,6-dimethyl-4-benzhydrylidene-2,5-cyclohexadien-1-one (*Ib*), m.p. 200–202°C (in agreement with the literature¹⁶) were prepared by the method described⁹. 2,6-Diethyl-4-benzhydrylidene-2,5-cyclohexadien-1-one (*Ic*) was prepared by oxidation of 2,6-diethyl-4-benzhydrylphenol using manganese dioxide in benzene under the conditions of ref.¹⁰, yield 82%, m.p. 166–167°C (acetone-methanol). For $C_{23}H_{22}O$ (314.4) calculated: 87.86% C, 7.05% H; found: 87.80% C, 6.98% H. 2,6-Diisopropyl-4-benzhydrylidene-2,5-cyclohexadien-1-one (*Id*), m.p. 171–172°C, (literature¹⁰ m.p. 170–171°C). 2,6-Di-*tert*-butyl-4-benzhydrylidene-2,5-cyclohexadien-1-one (*Ie*), m.p. 183 to 184°C, (in agreement with the literature¹¹). 2,6-Dibromo-4-benzhydrylidene-2,5-cyclohexadien-1-one (*If*), m.p. 238°C (literature⁸ m.p. 233°C). 2,6-Dimethoxy-4-benzhydrylidene-2,5-cyclohexadien-1-one¹² (*Ig*), m.p. 222–224°C, (literature¹² m.p. 225–226°C). 2,6-Di-*tert*-butyl-4-isopropylidene-2,5-cyclohexadien-1-one (*II*), m.p. 103–104°C (in agreement with the literature¹⁷) was prepared as described elsewhere¹³. 10-Methyleneanthrone (*IIIa*), m.p. 146–147°C, (literature¹⁴ m.p. 147–148°C). 10-Benzhydrylideneanthrone¹⁵, (*IIIb*) m.p. 204–206°C, (literature¹⁸ m.p. 208°C).

Physical measurements. Dipole moments in the ground state were determined from dielectric measurements of benzene solutions at 25°C using a heterodyne apparatus (frequency 1.2 Mc s⁻¹).

Usually five measurements were carried out in the concentration range $5 \cdot 10^{-3}$ – $5 \cdot 10^{-2}$ M. The overall polarizations P_2^0 were calculated according to Halverstadt and Kumler¹⁹ from the slopes α and β of the plots ϵ_{12} vs w_2 and d_{12}^{-1} vs w_2 , respectively. In the final calculation of μ , an allowance of 5% or 15% of the R_D values was made for atomic polarization. Molar refraction R_D was calculated from Vogel's increments²⁰ and the exaltation in the conjugated system estimated to 2 cm^3 in all the derivatives. This estimate is based on molar refractions of 1,4-pentadien-3-one²¹ and 3,5-hexadien-2-one²²; it may introduce an error of 0.02 D into the final dipole moment values, at worst. All the pertinent values are listed in Table I.

The excited state dipole moments were determined from solvent-induced spectral shifts. Electronic spectra were recorded on a Specord UV-VIS spectrophotometer (Zeiss, Jena) at a scan speed $16.7 \text{ cm}^{-1}/\text{s}$ in the solvents: n-hexane, isooctane, cyclohexane, tetrahydrofuran, dichloromethane, acetone and acetonitrile. The choice of solvents was restricted to non-interacting ones; ethanol causes the deviation from Eq. (2). The wavenumbers of the first $\pi \rightarrow \pi^*$ absorption band used for the study are listed in Table II; the extinction coefficients are given only for isooctane solvent. With one exception (see Notes to Table II) there were no problems with the assignment since there was only one band with $\epsilon > 1000$ between 20 to $30 \cdot 10^3 \text{ cm}^{-1}$.

The results were processed according to Eq. (2) by a program for multiple regression. The important statistics are listed in Table III. According to the multiple correlation coefficient the fit is satisfactory in all but one case. The dependence is graphically represented in Fig. 1A for a typical example, by plotting the two sides of Eq. (2) against each other. It is compared to the incorrect statistical procedure⁶ based on Eq. (1) (Fig. 1B).

TABLE I
Polarization Data of Quinone Methides I–III (Benzene, 25°C)

Compound	α^a	β^a	P_2^0 cm^3	R_D^b cm^3	μ (5%) ^c D	μ (15%) ^c D	$\nu(\text{C}=\text{O})^d$
Ia	13.72	−0.300	730.5	81.7	5.62 ^e	5.57	1 631.8
Ib	15.87	−0.258	929.1	901.0	6.38	6.35	1 615.0
Ic	12.67	−0.195	837.1	100.3	5.98	5.94	1 612.0
Id	7.55	−0.191	583.0	109.6	4.83	4.78	1 611.6
Ie	6.03	−0.167	527.7	118.9	4.44	4.37	1 611.0
If	14.94	−0.524	1 244.4	97.1	7.48	7.43	1 648.9
Ig	11.54	−0.274	772.5	94.7	5.74	5.70	1 647.8
II	9.30	−0.092	507.7	79.5	4.55	4.51	1 616.5
IIIa	6.90	−0.341	316.6	64.1	3.49	3.44	1 665.0
IIIb	4.64	−0.344	397.9	112.7	3.69	3.62	1 669.0

^a Slopes of the Halverstadt–Kumler¹⁹ plots; ^b estimated from increments, see Experimental; ^c correction for the atomic polarization of 5% or 15% of the R_D value, respectively; ^d in tetrachloromethane solution; ^e ref.⁴ gives 5.80 D at 32°C without correcting for P_A .

TABLE II
Solvent Effects on the First Absorption Maxima (10^3 cm^{-1}) of Quinone Methides I–III

Compound	n-Hexane	Cyclohexane	Isooctane ($\log \epsilon$)	Tetrahydrofuran	Dichloromethane	Acetonitrile	Acetone
<i>Ia</i>	28.00	27.75	27.90 (4.45)	27.00	26.60	26.80	26.90
<i>Ib</i>	27.40	27.35	27.35 (4.45)	26.70	26.60	26.90	26.95
<i>Ic</i>	27.50	27.30	27.45 (4.42)	26.65	26.80	27.10	27.00
<i>Id</i>	27.20	27.10	27.10 (4.43)	26.80	26.55	26.75	26.80
<i>Ie</i>	27.30	27.20	27.20 (4.41)	26.75	26.70	26.75	26.75
<i>If</i>	25.90	25.50	25.70 (4.42)	24.80	24.20	24.40	24.70
<i>Ig</i>	26.30	25.95	26.30 (4.42)	25.90	25.40	25.60	25.75
<i>II</i>	31.50	31.40	31.50 (4.45)	31.00	30.90	30.70	30.90
<i>IIIa^a</i>	36.75	36.65	36.65 (4.23)	36.10	36.25	36.25	36.25
<i>IIIb</i>	28.60	28.20	28.30 (3.95)	27.70	27.70	28.10	28.00

^a The values correspond to the second band since the first one in the region $29-30 \cdot 10^3 \text{ cm}^{-1}$ could not be exploited due to its low intensity.

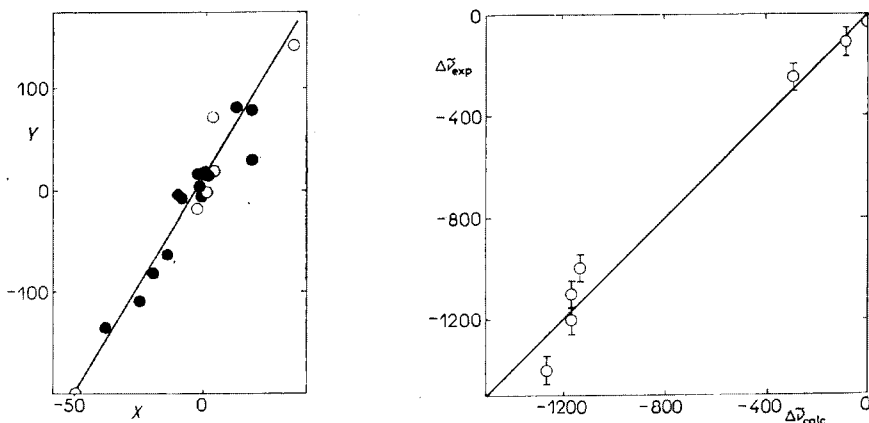


FIG. 1

Solvent Induced Spectral Shifts of 4-benzhydrylidene-2,5-cyclohexadien-1-one (*Ia*)

A The correct plot of the left-hand vs the right-hand side of Eq. (2). *B* The statistically incorrect plot⁶ based on Eq. (1) and using all the possible pairs of solvents; $Y = (\tilde{\nu}_j - \tilde{\nu}_i) / [f(n_i^2) - f(n_j^2)]$ plotted against $X = [f(\epsilon_i) - f(\epsilon_j)] / [f(n_i^2) - f(n_j^2)]$; ○ insignificant points with $[f(n_i^2) - f(n_j^2)]$ less than 0.01, ● other points.

The values of the coefficients B were used for calculation of $\Delta\mu$ and μ_e , assuming the collinearity of μ_g and μ_e . The final precision is further limited by the estimation of a_0 which was made as described⁷. The values of a_0 as well as the resulting values of $\Delta\mu$ and μ_e are listed in Table III.

The infrared absorption spectra were recorded on a Perkin Elmer 60120 spectrophotometer in a 0.1 mm cell. The concentration of the tetrachloromethane solution was 0.03M. The carbonyl frequencies are listed in Table I.

DISCUSSION

Let us start the discussion with the ground state dipole moments of *IIIa,b*. When compared to the moment of anthrone^{2,3} (3.66 D) they do not reveal any additional conjugation and suggest that the compounds *IIIa* and *IIIb* are to be viewed as simple aromatic ketones; the contribution from the formula B is not detectable. Even the presence of two phenyl groups in *IIIb* has but a small effect. These results were expected since the weak quinone character of 10-methyleneanthrone (*IIIa*) and its principal difference from other quinone methides has been noted³.

On the other hand, the dipole moments of fuchsone (*I*) and its derivatives are significantly higher. A comparison of *I* to benzophenone revealed the increment of 2.6 D and the contribution of the formula B was estimated⁴ to 10%; according to our results this share would be between 9 and 18% for the compounds *Ia–Ig*

TABLE III
Statistics of Eq. (2) and Excited State Dipole Moments of Quinone Methides *I–III*

Compound	R^a	B^b cm ⁻¹	C^b cm ⁻¹	a_0 Å	$\Delta\mu$ D	μ_e D
<i>Ia</i>	0.989	4 496 (329)	29 (71)	3.9	4.8	10.3
<i>Ib</i>	0.966	2 491 (337)	85 (74)	4.1	2.7	9.0
<i>Ic</i>	0.956	2 341 (369)	57 (81)	4.2	2.9	8.8
<i>Id</i>	0.962	1 781 (252)	12 (55)	4.4	3.2	7.9
<i>Ie</i>	0.996	2 072 (95)	- 7 (21)	4.5	4.3	8.7
<i>If</i>	0.972	5 066 (617)	-19 (134)	4.1	4.7	12.1
<i>Ig</i>	0.901	2 381 (574)	4 (125)	4.1	2.9	8.5
<i>II</i>	0.985	2 401 (222)	- 74 (48)	4.0	3.4	7.9
<i>IIIa</i>	0.965 ^c	1.952 ^c (268)	- 8 ^c (58)	3.6	2.6 ^c	6.1 ^c
<i>IIIb</i>	0.979	2 308 (256)	-57 (56)	4.3	4.9	8.6

^a Multiple correlation coefficient; ^b coefficients of Eq. (2) with their standard deviations (in parentheses); ^c these values are not comparable with the others, see Note^a, Table II.

respectively. In the case of 7,7-ethylenedimercapto derivatives of quinone methides the contribution of the polar form was estimated to 15–17% by similar reasoning⁵; the opposite behaviour of the 10-methyleneanthrone derivative was also observed⁵. All such figures are, of course, little theoretically founded on the one hand and very approximate on the other hand since they depend on the crude estimates of dipole moments predicted for the two idealized forms, see formulae *A*, *B*.

In a recent discussion of the possible aromatic character of tropone it was argued²⁴ that its dipole moment 4.30 D is no evidence in favour of the dipolar formula, since the dipole moment of 2,6-cycloheptadienone (4.04 D) is not significantly lower and at the same time distinctly higher than the moments of simple ketones. A part of the enhancement may thus be explained by electrostatic induction in the highly polarizable π -electron system. When applying this reasoning to our compounds, we may refer again to 2,6-cycloheptadienone since 2,5-cyclohexadienone is not available. The comparison shows still an additional mesomeric moment and one may conclude that the dipolar formula *B* is of importance even when its exact contribution cannot be estimated.*

The most interesting feature of Table III are the striking differences between the individual alkyl derivative *Ia–e*. The only reasonable explanation assumes that the sterically pretentious alkyl groups hinder the coplanarity of the conjugated system; even a small distortion may be significantly manifested in the dipole moment values. The unsubstituted fuchsone (*Ia*) deviates from the sequence, even when a correction for the moments of the alkyl groups (0.3 D) is applied. Hence these alkyl groups must exhibit still another effect than purely steric. The extent of conjugation may be also estimated from the carbonyl frequency (less double bond character and shift to the lower wave numbers) or from the electronic spectra (bathochromic shift). The results from the three quantities are concordant only as far as the unsubstituted fuchsone is compared with its alkyl derivatives: the conjugation is strengthened by substitution. The much smaller differences between the individual alkyl derivatives themselves are reflected in the carbonyl frequency on the one hand, and in the ground state dipole moment on the other hand, in the opposite sense; the differences in the electronic absorption maxima are too small to be really significant.

The dipole moment of the dibromo derivative *If* includes the moments of the two C—Br bonds; after correcting for this contribution (subtraction of 1.58 D) it is comparable to the diethyl derivative *Ic*. The moment of the dimethoxy derivative *Ig* cannot be discussed in terms of conjugation due to the unknown conformation on the two C—O bonds. In contrast to the importance of substitution in the posi-

* When discussing the dipole moments of the molecules *I–III*, one must take into consideration that some similar compounds exhibit anomalous moments which are explained most probably by solvent effects²⁵. For example, the dipole moment of *p*-quinone is definitively non-zero²⁵. However, the values of Table I are high enough to make this effect unimportant.

tion 2, 6, the substituents in position 7 seem to be almost without influence on dipole moments, as follows from the comparison of compounds *II* and *Ie*.

The dipole moments in the excited state must be discussed with caution owing to their rather approximate character. The main source of the inaccuracy is the inherent imperfection of the theory. As far as the overall fit is concerned, the multiple correlation coefficient is higher than 0.95 in all cases except *Ig*. The theoretical postulate of zero intercept is also fulfilled. However, a closer analysis reveals that Eq. (2) is not well founded since the first term on the right-hand side is almost insignificant. Only the dependence of solvent shifts on the dielectric constant has been actually verified, the dependence on the refraction index has remained merely the theoretical postulate. This fact has been obscured by the incorrect statistical treatment⁶, see Fig. 1*B*. In our opinion, all the theories connecting solvent induced shifts with excited state moments should be reexamined by the correct statistics on a broader experimental material. For the time being let us discuss the values obtained as approximate estimates.

According to a theoretical study of some simpler derivatives², the first excited state corresponds to a singlet to singlet transition of the $\pi \rightarrow \pi^*$ type with the symmetry ${}^1A_1 \rightarrow {}^1A_1$; the polarization proceeds along the symmetry axis. For some derivatives the ${}^1A_1 \rightarrow {}^1B_1$ bands in the same region were also predicted² but they cannot interfere due to their low intensity ($\epsilon < 100$). In agreement with the theoretical prediction all the excited state dipole moments are significantly higher than in the ground state; this behaviour is typical^{6,26} particularly for conjugated systems with the dipole moments in their long axis unless there is an appreciable charge separation already in the ground state. Qualitatively it was also predicted by CNDO/S calculations²⁷ on the parent substance, 4-methylene-2,5-cyclohexadienone; these calculations anticipated the values of 4.69 D and 6.25 D for the ground state and first excited state, respectively. Simple aromatic ketones show but slightly enhanced dipole moments in the excited state²⁶, in average by 0.5 D. Hence even the excited state dipole moments of quinone methides agree with the assumption of a strong conjugation. One may state that the mesomeric formula *B* contributes more to the first excited state than to the ground state; with the provision already mentioned this contribution may be estimated to 25–40% for individual compounds studied. When these compounds are compared to each other, the salient feature is that many differences marked in the ground state are smoothed out. In particular the anthrone derivative *IIIb* differs no more significantly from benzoquinone derivatives; the difference between fuchsone (*Ia*) and its alkyl derivatives *Ib*–*Ie* still persists but these alkyl derivatives themselves do not virtually differ. An anomalously high moment of the dibromo derivative *If* cannot be understood without comparison to further derivatives.

In conclusion we may state that the conjugation within the quinone methide system is significant and is reflected in various physical quantities including dipole moments,

carbonyl frequencies, electronic absorption maxima, although the results from different quantities are not quite consistent. Since more exact physical methods have not yet been applied (except an unfinished X-ray study²⁸) a quantitative estimation of this conjugation is not yet possible.

Thanks are due to Mrs M. Kuthanová, Institute of Chemical Technology, Prague for measuring the dielectric constants and densities and to Dr S. Vašíčková from this Institute for recording the infrared spectra.

REFERENCES

1. Pospíšek J., Pišová M., Souček M., Exner O.: This Journal 40, 2093 (1975).
2. Musil L., Pišová M., Pospíšek J., Souček M.: This Journal, in press.
3. Wagner H.-U., Gompper T. in the book: *The Chemistry of the Quinonoid Compounds* (S. Patai, Ed.), p. 1145. Interscience, London 1974.
4. Maryott A. A., Acree S. F.: J. Res. Nat. Bur. Stand. 38, 505 (1947).
5. Gompper R., Schmidt R. R., Kutter E.: Justus Liebigs Ann. Chem. 684, 37 (1965).
6. Varma C. A. G. O., Groenen E. J. J.: Rec. Trav. Chim. Pays-Bas 91, 296 (1972).
7. Edward J. T.: Chem. Ind. (London) 1956, 774.
8. Auwers K., Schröter O.: Ber. Deut. Chem. Ges. 36, 3253 (1903).
9. Pospíšek J., Pišová M., Souček M.: This Journal 40, 142 (1975).
10. Becker H.-D.: J. Org. Chem. 32, 2943 (1967).
11. Becker H.-D.: J. Org. Chem. 32, 2115 (1967).
12. Benyon K. B., Bowden S. T.: J. Chem. Soc. 1957, 4247.
13. Koutek B., Pavlíčková L., Souček M.: Syn. Commun., in press.
14. Starnes W. H. jr: J. Org. Chem. 35, 1974 (1970).
15. Padova M. R.: C. R. Acad. Sci. 143, 121 (1906).
16. Becker H.-D.: J. Chem. Soc. 32, 2124 (1967).
17. Cook C. D., Norcross B. E.: J. Amer. Chem. Soc. 78, 3797 (1956).
18. Bergmann E.: Ber. Deut. Chem. Ges. 63, 1037 (1930).
19. Halverstadt I. F., Kumler W. D.: J. Amer. Chem. Soc. 64, 2988 (1942).
20. Vogel A. I.: J. Chem. Soc. 1948, 1842.
21. Nazarov I. N., Torgov I. V.: Izv. Akad. Nauk SSSR, Otd. Khim. Nauk 1947, 495.
22. Pudovik A. N.: Izv. Akad. Nauk SSSR, Otd. Khim. Nauk 1948, 529.
23. Vasileva V. N., Bazov V. P., Geiderikh M. A.: Zh. Fiz. Khim. 33, 1516 (1959).
24. Bertelli D. J., Andrews T. G.: J. Amer. Chem. Soc. 91, 5280 (1969).
25. Nagai T., Takahashi H., Higasi K., Sutton L. E., Waddington D.: Bull. Chem. Soc. Jap. 47, 3010 (1974).
26. Bakhshiev N. G., Knyazhanskii M. I., Minkin V. I., Osipov O. A., Saidov G. V.: Usp. Khim. 38, 1644 (1969).
27. Musil L., Souček M.: Unpublished results.
28. Racine-Weisbuch M.: C. R. Acad. Sci., Ser C. 269, 99 (1969).

Translated by the author (O. E.).