[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Behavior of 1,2-Diketones at the Dropping Mercury Electrode[1]

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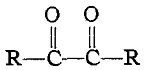
The reduction of a number of cyclic and acyclic 1,2-diketones at the dropping mercury electrode has been studied. The half-wave potentials of the acyclic 1,2-diketones I are found to be shifted to more negative potentials as the degree of alkyl substitution at the α-carbons is increased. It is proposed that the increasing α-substitution offers increasing "insulation" of the dicarbonyl system from the electrode and increasing steric hindrance to *trans* coplanarity of the dicarbonyl system. On the basis of the half-wave potentials determined for the cyclic 1,2-diketones II, it is suggested that these values are influenced by the degree of coplanarity of the dicarbonyl system allowed by the ring size and the hindrance of the α-methyl groups. The ultraviolet and infrared absorption maxima for the acyclic 1,2-diketones are reported and correlated where possible with the ease of reduction of the dicarbonyl system.

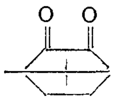
It has been shown, in an examination of camphorquinone (II) and a series of 3,3,*n*,*n*-tetramethyl-1,2-cycloalkanediones III, that the position of the long wave length (337–466 mμ) ultraviolet absorption band is a function of the angle between the planes of the carbonyl groups.[2] It was of interest to study the reduction of these 1,2-cycloalkanediones at the dropping mercury electrode in order to detect any dependence of reduction potential upon the steric configuration of the carbonyl groups. As a necessary introduction to this study, the polarographic reduction potentials of a series of acyclic 1,2-diketones I were measured to determine the influence of degree of α-alkyl substitution upon the ease of reduction at the dropping mercury electrode. Only the first compound in this series, diacetyl (Ia), had been investigated previously for its polarographic reduction behavior. The most recent study, by Harrison,[3] showed only one wave for the reduction of diacetyl, contrary to the findings of other workers,[4,5] and indicated the necessity of carrying out the polarographic reduction of diacetyl in buffered solution in order to obtain reliable results.



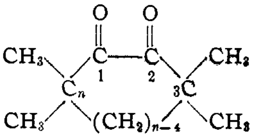
$R-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-R$

I

a, R = CH_3
b, R = $CH_2CH_2CH_3$
c, R = $CH(CH_3)_2$
d, R = $C(CH_3)_3$



II



III

a, *n* = 6
b, *n* = 7
c, *n* = 8
d, *n* = 18

Experimental

Apparatus.—The polarographic measurements were carried out with a Sargent Model XXI Automatic Recording Polarograph. The polarographic cell used was of the H-type.[6] The dropping mercury electrode delivered 1.118 mg. of mercury per second at a reservoir height of 64 cm. The drop time was found to be 5.0 seconds and the capillary constant, $m^{2/3}t^{1/6}$, was 1.41 mg.$^{2/3}$sec.$^{-1/2}$. The solvent was 50% (by volume) isopropyl alcohol–water. Buffer 1 was 0.1 *M* in chloroacetic acid and 0.1 *M* in sodium chloroacetate. The *p*H, as measured with a glass electrode, was 3.5. Buffer 2 was 0.1 *M* in acetic acid and 0.1 *M* in sodium acetate; the measured *p*H was 5.6. Buffer 3 was 0.01 *M* in sodium hydroxide and 0.03 *M* in monopotassium phosphate; *p*H 12. All measurements were made at 25°. All solutions were bubbled with purified nitrogen before the polarographic measurements were made. The voltage was measured *versus* the saturated calomel electrode (S.C.E.). The polarography of camphorquinone (II) was carried out in the three buffer solutions to determine the effect of *p*H on the half-wave potential. Buffer solution 2 was used in all subsequent measurements. The effect of variation in the height of the mercury reservoir on the diffusion current was determined.[7]

The ultraviolet absorption spectra were determined using solutions of the compounds in freshly distilled 95% ethanol and employing a Cary Automatic Recording Spectrophotometer, Model 11.

The infrared absorption spectra were determined using thin films of the pure liquid compounds. The spectral curves were recorded by a Perkin–Elmer Infrared Spectrometer, Model 12B, having rock salt optics.

Chemicals.—Diacetyl (Eastman Kodak Co.) was purified by distillation. The cyclic 1,2-diketones III and dipivaloyl (Id) have been described previously; only 3,3,8,8-tetramethyl-1,2-cyclooötanedione (IIIc) was less than analytically pure.[2] Dibutyl and diisobutyryl were prepared as outlined below.

Diisobutyryl.—The procedure of Wegmann and Dahn[8] was modified as follows. A solution of 15 g. of isobutyroin, b.p. 85–90° (30 mm.),[9] 40 g. of ferric chloride and 100 ml. of 95% ethanol was heated under reflux for 7 hours. The reaction mixture was extracted with ether, and the ether extract was washed three times with saturated calcium chloride solution. The ethereal solution was dried over anhydrous sodium sulfate, the ether was removed, and the product was distilled, b.p. 63.5–64.5° (31 mm.), $n^{20}\text{D}$ 1.4108,[10] yield 10 g. (70%).

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.56; H, 9.92. Found: C, 67.37; H, 9.96.

Dibutyryl.—The compound was obtained from butyroin, b.p. 103–105° (20 mm.),[9] by the procedure of Wegmann and Dahn,[8] b.p. 71–72° (24 mm.), $n^{20}\text{D}$ 1.4180, d^{20}_4 0.910.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.56; H, 9.92; *MR*D, 39.18. Found: C, 67.26; H, 9.94; *MR*D, 39.36.

Discussion

In Table I are recorded the data for the polarographic reduction of the 1,2-diketones I, II and III: the half wave potentials, wave heights and reciprocal slopes of the plots of log $(i_d - i)/i$ *versus E*. To establish the type of process occurring at the dropping mercury electrode, the height of the mercury reservoir was varied. In a diffusion controlled process the current is proportional to the

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[1] This investigation was supported by a grant from E. I. du Pont de Nemours and Company, Inc.

[2] N. J. Leonard and P. M. Mader, THIS JOURNAL, **72**, 5388 (1950).

[3] S. Harrison, *Collection Czech. Chem. Communs.*, **15**, 818 (1950).

[4] A. Winkel and G. Proske, *Ber.*, **69**, 1917 (1936).

[5] H. Adkins and F. W. Cox, THIS JOURNAL, **60**, 1151 (1938).

[6] J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

[7] I. M. Kolthoff and J. J. Lingane, "Polarography," Second Edition, Interscience Publishers, Inc., New York, N. Y., 1952, p. 85.

[8] J. Wegmann and H. Dahn, *Helv. Chim. Acta*, **29**, 101 (1946).

[9] J. M. Snell and S. M. McElvain, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 114.

[10] Compare $n^{20}\text{D}$ 1.42057 (W. N. Krestinski and L. I. Baschenowa-Koslowskaja, *Ber.*, **66**, 97 (1933)).

TABLE I

POLAROGRAPHIC REDUCTION OF 1,2-DIKETONES

Compound	pH	Concn.,[a] mM	Wave height, μa.	$-E_{1/2}$[c] vs. S.C.E., v.	Reciprocal slope
Diacetyl (Ia)	5.6[b]	1.14	2.42	0.81[d]	0.076
	5.6	1.14	2.26	.81	.070
Dibutyryl (Ib)	5.6	1.23	2.83	.83	.073
	5.6	1.23	2.80	.83	.075
	5.6	1.23	2.59	.82	.070
Diisobutyryl (Ic)	5.6	1	1.65	.87	.070
	5.6	1.25	2.66	.89	.074
Dipivaloyl (Id)	5.6	1	1.59	1.27	.11
	5.6	0.74	1.20	1.28	.12
Camphorquinone (II)	3.5	1	2.11	0.68	.061
	5.6	1	2.28	0.76	.061
	12	1	1.50	1.00	.067
3,3,6,6-Tetramethyl-1,2-cyclohexanedione (IIIa)	5.6	1	2.14	0.71	.063
	5.6	1	2.15	0.71	.061
3,3,7,7-Tetramethyl-1,2-cycloheptanedione (IIIb)	5.6	1	2.79	1.12	.087
	5.6	1	2.90	1.13	.086
	5.6	1	2.79	1.13	.086
3,3,8,8-Tetramethyl-1,2-cycloöctanedione (IIIc)	No reduction				
3,3,18,18-Tetramethyl-1,2-cycloöctadecanedione (IIId)	5.6	1	0.70	1.21	0.091

[a] Solvent, 50% isopropyl alcohol–water. [b] Buffer for pH 5.6 was 0.1 M HOAc + 0.1 M NaOAc. [c] Not corrected for liquid junction potentials; this correction would be common to all $E_{1/2}$ values. [d] Compare −0.93 v. *vs.* mercury pool in ammonium chloride[5]; −0.82 v. *vs.* S.C.E. in aqueous KCl[11]; −0.86 v. in aqueous sodium sulfite[12]; −0.64 at pH 5.7 in water.[3]

height of the mercury reservoir, $i_d = Kh_{\text{cor}}^{1/2}$. The results obtained with 3,3,6,6-tetramethyl-1,2-cyclohexanedione (IIIa) are given in Table II, and from the calculations it is apparent that the process in the reduction is diffusion controlled. The same conclusion can be reached by an examination of the data of Harrison[3] for i_d *vs.* $h_{\text{cor}}^{1/2}$ in the polarographic reduction of diacetyl (Ia).

TABLE II

EFFECT OF CHANGE OF HEIGHT OF MERCURY RESERVOIR ON VALUE OF DIFFUSION CURRENT WITH 3,3,6,6-TETRAMETHYL-1,2-CYCLOHEXANEDIONE

Height of reservoir, cm.	Diffusion current, i_d, μa.	$i_d/h_{\text{cor}}^{1/2}$
62.6	2.33	0.295
52.6	2.11	.291
42.6	1.97	.301

TABLE III

CALCULATION OF DIFFUSION COEFFICIENTS OF 1,2-DIKETONES[a]

Diketone	I	$D \times 10^6$, cm.^{2}/sec. $n = 1$	$n = 2$
Diacetyl (Ia)	1.5	6.1	1.5
Dibutyryl (Ib)	1.6	7.0	1.7
Diisobutyryl (Ic)	1.5	6.1	1.5
Dipivaloyl (Id)	1.1	3.3	0.83
Camphorquinone (II)	1.6	7.0	1.7
3,3,6,6-Tetramethyl-1,2-cyclohexanedione (IIIa)	1.5	6.1	1.5
3,3,7,7-Tetramethyl-1,2-cycloheptanedione (IIIb)	2.0	11	2.7
3,3,18,18-Tetramethyl-1,2-cyclooctadecanedione (IIId)	0.5	0.68	0.17

[a] Solvent, 50% isopropyl alcohol–water; buffer, 0.1 M HOAc + 0.1 M NaOAc, pH 5.6; $I = i_d/Cm^{2/3}t^{1/6}$.

To establish the number of electrons (n) involved in the reduction, the diffusion coefficients (D) were calculated from the Ilkovic equation, $I = 605\ nD^{1/2}$, where $I = i_d/Cm^{2/3}t^{1/6}$, C is the concentration of the reducible substance, and $m^{2/3}t^{1/6}$ the capillary constant. In Table III the I values and the values calculated for the diffusion coefficients, assuming one and two electrons involved in the reduction process, are summarized. The diffusion coefficient of the closely related substance, camphor, at 20° in 96% ethanol, concentration 0.5 M, has been found to be 6.8×10^{-6} cm.^{2}/sec.[13] This value compares favorably with the calculated value for camphorquinone (II) (*i.e.*, 7.0×10^{-6} cm.^{2}/sec.) if a one-electron process is assumed. The values of the reciprocal slope of the plot of log $(i_d - i)/i$ *vs.* E (see Table I) indicate that the one-electron process at the electrode is not reversible. It will be noted from Table I that, in general, the reciprocal slope becomes greater with increasing half-wave potential, indicating greater departure from reversibility with increasing difficulty of reduction.

Other findings on the polarographic reduction of related ketones have indicated a one-electron process. Thus, Coulson and Crowell,[14] on the basis of the polarography of unsaturated and aromatic carbonyl compounds suggested, and offered theoretical arguments for, a one-electron one-proton process. Also, Fields and Blout,[15] from a systematic study of the polarographic reduction of a series of unsaturated aldehydes, concluded that the reduction of these aldehydes is a one-electron process, *i.e.*, the product in each case is that of a bimolecular reduction. There are a number of examples of the bimolecular "chemical" reduction of 1,2-dicarbonyl compounds. Thus, it was found by von Pechmann[16] that the reduction of diacetyl with zinc and sulfuric acid gave the coupling product, or diketopinacol, and by Fuson and his coworkers[17] that the reduction of t-butyl glyoxal with the binary mixture magnesium–magnesium iodide in benzene–ether gave 1,2-dipivaloylethylene glycol. Conant and Cutter[18] found that 1,2-diketones can be reduced readily with titanous chloride, which suggests a one-electron or bimolecular reduction, as found with certain carbonyl compounds and vanadous or chromous salts.

Further discussion of the polarographic reduction of the 1,2-diketones I, II and III is based upon the

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[11] E. I. Fulmer, J. J. Kolfenbach and L. A. Underkofler, *Ind. Eng. Chem., Anal. Ed.*, **16**, 469 (1944).

[12] L. A. Greenberg, *J. Biol. Chem.*, **147**, 11 (1943).

[13] *International Critical Tables*, **5**, 74 (1929).

[14] D. M. Coulson and W. R. Crowell, THIS JOURNAL, **74**, 1290 (1952); **74**, 1294 (1952).

[15] M. Fields and E. R. Blout, *ibid.*, **70**, 930 (1948).

[16] H. von Pechmann, *Ber.*, **21**, 1411 (1888); *ibid.*, **22**, 2214 (1889).

[17] R. C. Fuson, C. H. McBurney and W. E. Holland, THIS JOURNAL, **61**, 3246 (1939).

[18] J. B. Conant and H. B. Cutter, *ibid.*, **48**, 1016 (1926).

conclusions reached thus far, that their reduction at the dropping mercury electrode is a diffusion controlled, one-electron process. The half-wave potentials of the acyclic diketones I will be considered first. The difference in these molecules is in the degree of alkyl substitution at the α-carbons. Since the *trans* configuration for the 1,2-dicarbonyl system is believed to be favored in the acyclic diketones[19] the observed variation in the half-wave potentials is probably due to the steric environment of the dicarbonyl system, including any steric resistance to *trans* coplanarity. The shift in half-wave potentials from that of diacetyl (Ia) appears to be a logarithmic function of the number of alkyl substituents on a α-carbon (1 alkyl substituent (Ib), -0.02; 2 (Ic), -0.07; 3 (Id), -0.47). In order to visualize the effect of the steric environment of the dicarbonyl system on the half-wave potential of the diketone, the behavior of the compound near and at the electrode should be considered. In Fig. 1 (A to E) is indicated pictorially what is believed to be happening at the electrode. The non-polarized diketone molecule is shown at the electrode surface in A. At the electrode surface the dicarbonyl system is polarized (B). If only one carbonyl were involved in the polarization and reduction, the diketone would behave essentially as a monoketone, and monoketones are known to be reduced with much greater difficulty at the dropping mercury electrode.[4,20] The addition of an electron at one extreme of the dicarbonyl system, accompanied by the capture of a proton at the other extreme (C), is here visualized as an extension of the formulation by Coulson and Crowell[14] for a one-electron one-proton process, and is analogous to the bimolecular reduction, at the dropping mercury electrode, of mesityl oxide.[21] The radical (D) formed by the addition of the electron is stabilized by resonance (E is a contributing species), and can then undergo coupling to give a bimolecular reduction product (diketopinacol).

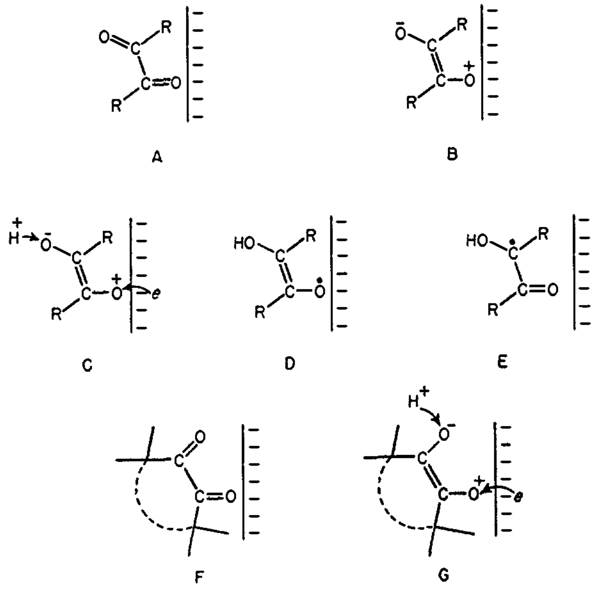

Fig. 1.—Behavior of diketones at the electrode.

In order to exist as the polarized form (C), the most favorable configuration of the dicarbonyl portion of the molecule will be coplanar. For the acyclic diketones I, the half-wave potential appears to depend upon the tendency of the dicarbonyl system to assume coplanarity and upon the availability of this system at the electrode (C). The α-methyl groups in dipivaloyl (Id) may "insulate" or "shield" the dicarbonyl system from the electrode. However, at a sufficiently negative potential, the attraction between the polarized form of the diketone molecule and the electrode is great enough to overcome the hindrance of the methyl groups, and the dicarbonyl system is able to reach the electrode to react. The "insulating" effect would be expected to be less in Ic and less again in Ib, and the half-wave potentials are in this order (Table I).

The cyclic diketones can be discussed under a scheme similar to that for the acyclic diketones. Instead of a *trans* configuration, a *cis* configuration is necessary for II, IIIa, IIIb and IIIc. In Figs. 1F and G are represented the *cis* non-polarized and polarized forms of the cyclic 1,2-diketones. If reaction is to take place at the extremes of the diketone system, the ease of accommodation of the double bond in the ring would be expected to be an important factor in determining the potential at which reduction takes place. Compounds II and IIIa (the five- and six-membered rings) were found to have the most positive half-wave potentials, IIIb was reduced with much greater difficulty, and IIIc was found not to reduce under the conditions employed. The construction of scale molecular models of IIIa, b and c shows that the formation of the double bond, as indicated in G, becomes increasingly difficult in this order (six-, seven-, eight-membered rings) because of the increasing hindrance of the α-methyl groups and the alkylene chain to the parallel conformation required by a *cis* double bond. Thus, for the cyclic diketones (II, IIIa, b, c), the half-wave potential appears to be determined by the ease of formation of this reactive species at the electrode. The "insulation" of the dicarbonyl grouping from the electrode by the α-methyl groups is nearly equivalent for these cyclic ketones of 5–8 members (based upon models of the extreme polar form) and of a much lower order of effectiveness than that for dipivaloyl (Id). By contrast, the dicarbonyl system in 3,3,18,18-tetramethyl-1,2-cyclooöctadecanedione (IIId) favors the *trans* coplanar configuration, and the polarized *trans* form (similar to B in Fig. 1) should resemble that for dipivaloyl, especially in the "insulation" offered by the α-methyl substituents. It is not surprising, therefore, to find that the half-wave reduction potentials of Id and IIId are very similar.

It has been stated, as the result of an investigation, by Winkel and Proske,[4] of the effect of various substituents on the polarographic reduction potential of the carbonyl group, that there appears to be a parallelism between the half-wave potential and the wave length of the absorption maximum in the

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(19) J. E. LuValle and V. Schomaker, *ibid.*, **61**, 3520 (1939).

(20) M. Shikata and I. Tachi, *Collection Czech. Chem. Communs.*, **10**, 368 (1938).

(21) R. Pasternak, *Helv. Chim. Acta*, **31**, 753 (1948); see also pp. 664, 665 in ref. 7.

ultraviolet. As the absorption maximum was shifted toward longer wave lengths, the reduction potential was shifted to more positive values. It was therefore of interest to learn if this was a valid generalization that would be applicable to the diketones here studied. The ultraviolet absorption of the cyclic 1,2-diketones (II and III, also Id) was the subject of a previous study,[2] and the absorption maxima (both ultraviolet and infrared) of the acyclic diketones I are recorded in Table IV. The ultraviolet absorption maxima designated as B-bands are identified as those associated with the activation of the individual carbonyl groups and those designated as A-bands are those due to the activation of the 1,2-dicarbonyl grouping. Since it is the dicarbonyl grouping which is undergoing polarographic reduction, the half-wave potentials should be compared with the wave lengths of the A-bands. For the compounds: diacetyl (Ia), dibutyryl (Ib), diisobutyryl (Ic), the ultraviolet absorption maxima shift toward longer wave length (417 → 425 → 434 mμ) whereas the half-wave potentials are shifted toward more negative values (−0.81 → −0.83 → −0.88 v.), which relation is opposite to the Winkel and Proske prediction. Nevertheless, it will be noted that for dipivaloyl (Id) the wave length of the A-band is at its lowest value for the series (365 mμ) and this is the most difficult of the acyclic diketones to reduce at the dropping mercury electrode ($E_{1/2} = -1.27$ v.). The discontinuity, at dipivaloyl, of the apparently regular bathochromic effect of increasing α-alkyl substitution[22] probably results from a departure in Id from the coplanar *trans* configuration (Ia, b, c), caused by steric hindrance of the six methyl groups. The steric inhibition of dicarbonyl coplanarity in dipivaloyl is thus indicated by both ultraviolet absorption and polarographic data. The position of the A-band[2] and the half-wave potential do not bear any consistent relation for the cyclic 1,2-diketones (II, III), and the position of the infrared C=O absorption band bears no simple relation to the ease of polarographic reduction for I, II and III. Finally, in consideration of the bathochromic effect, on the carbonyl ultraviolet absorption maximum (B-band), of increasing α-alkyl substitution in the 1,2-diketones Ib, Ic, Id, it will be observed that this is parallel to the absorption behavior of the corresponding monoketones: methyl propyl ketone ($\lambda_{\max.}$ 281.4 mμ in hexane), methyl isopropyl ketone (284.5 mμ), and methyl *t*-butyl ketone (286.8 mμ).[23,24]

TABLE IV

ULTRAVIOLET AND INFRARED ABSORPTION MAXIMA

	Ultraviolet[a] A-band		B-band		Infrared[b] frequency, cm.$^{-1}$
1,2-Diketone	λ, mμ	ε	λ, mμ	ε	
Diacetyl (Ia)[c]	417	9.5	286	24.3	1720(s)[d]
					1713(s)
					1708(s)
Dibutyryl (Ib)	425	14.5	268	46.3	1710(s)
			266	46.1	3412(w)[e]
			264	45.6	
Diisobutyryl (Ic)	434	18.7	272	52.8	1713(s)
			268	52.3	3406(w)
			266	51.4	
Dipivaloyl (Id)[2]	365	21.0	294	47.0	1700(s)
			285	52.5	3376(w)
			~275	38	

[a] In 95% ethanol. [b] Pure liquid. [c] See ref. 7 in N. J. Leonard, R. T. Rapala, H. L. Herzog and E. R. Blout, THIS JOURNAL, **71**, 2997 (1949). [d] (s) indicates high intensity; (w) low intensity. [e] L. Marion, D. A. Ramsay and R. N. Jones, THIS JOURNAL, **73**, 305 (1951), have shown that for carbonyl groups which produce strong absorption bands in the region 1780–1620 cm.$^{-1}$, weak overtone bands may be expected at approximately twice this frequency range, *viz.*, 3560–3240 cm.$^{-1}$. See also ref. 2, this paper.

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(22) It has been suggested previously[2] that the maximum for a theoretical pure *trans*-α,α,-hexaälkyldiketone should lie closer to that for camphorquinone (466 mμ).

(23) K. L. Wolf, *Z. physik. Chem.*, **2**, 39 (1929).

(24) H. L. Donle and G. Volkert, *ibid.*, **8**, 60 (1930).